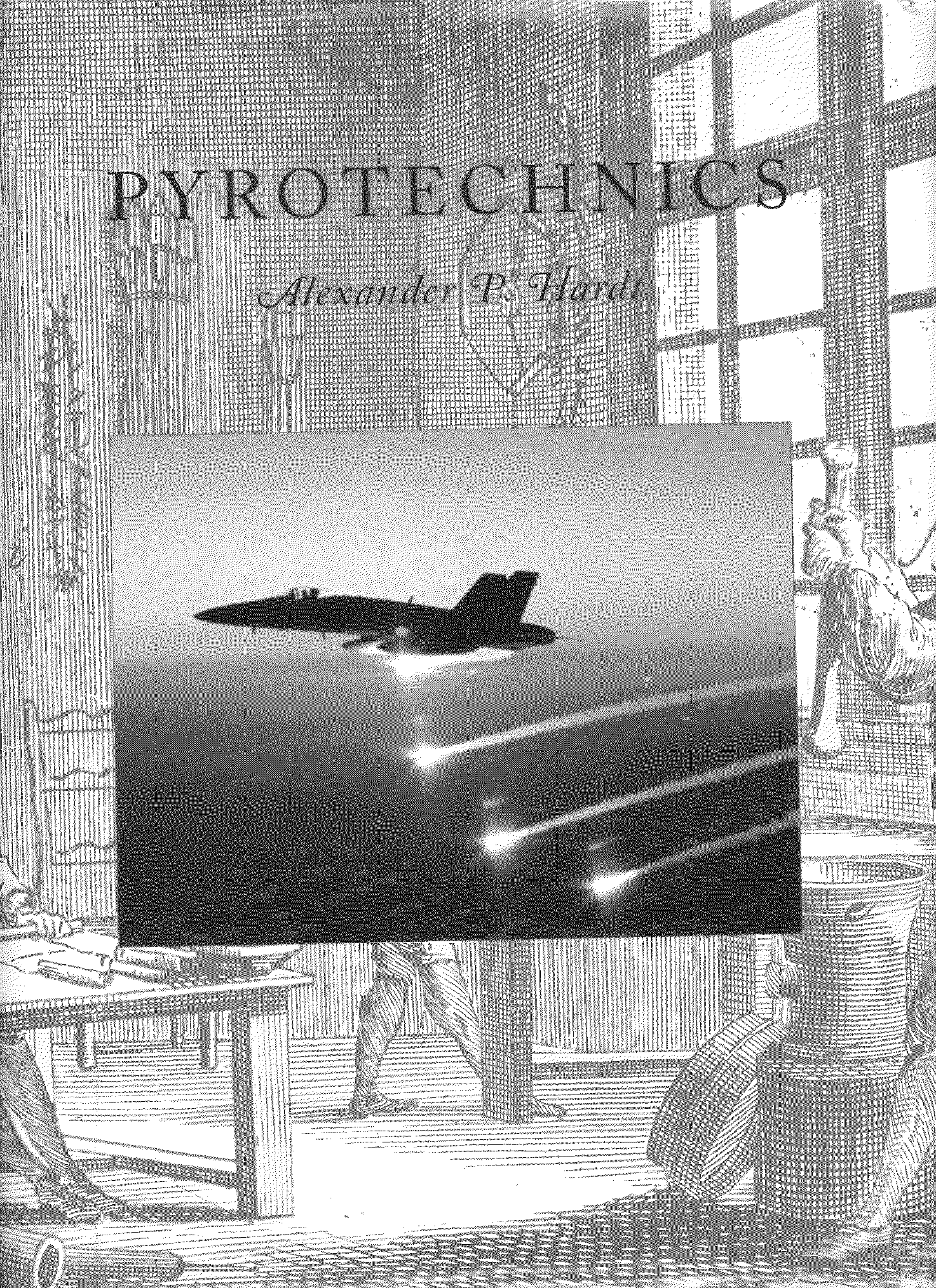
PYROTECHNICS

Alexander P. Hardt



Alexander P. Hardt
1930–1989

PYROTECHNICS

by

ALEXANDER P. HARDT, PH.D.

with contributions by

BARRY L. BUSH
on "Fireworks"

and

BARRY T. NEYER, PH.D.
on "Statistical Test and Analysis Methods"

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Publisher's Preface

In the history of the literature of pyrotechny, this is certainly not the first time a work has been posthumously published. The very first printed book on this subject, the *Pirotecnia* of Vannoccio Biringuccio (1480-1539), appeared in 1540. The first American work on the subject, *A System of Pyrotechny*, by James Cutbush (1788-1823), was published in 1825. That task fell to his widow Clara.

Another significant example is the first work to treat pyrotechnics from the "scientific" or quantitative approach, rather than the empirical, the *Lehrbuch der Pyrotechnik* of Prussian artillery officer Moritz Meyer (1798-1838), published at Berlin in 1840. More recently, *Pyrotechnics* by George W. Weingart was reissued twenty years after its author's death in 1948, and, most recently, Dr. Herbert Ellern's *Military and Civilian Pyrotechnics* (1968) has been reprinted by the original publisher many years after that author's death.

Regrettably, Dr. Hardt died suddenly only a few weeks after completing the first draft of his manuscript. This rested for a rather long time with a large publisher, and eventually Alex's widow, Peggy Hardt, retrieved the manuscript and requested that I see the manuscript to publication. It has not been exactly an easy task for me, and being a small specialty publisher, it did take quite some time to track down the funding and to assemble a group of very competent editors.

I should like to thank Dr. Takeo Shimizu, a good personal friend of Dr. Hardt, who was the very first person to review the manuscript. Dr. Shimizu also gave a very generous financial gift to help with the publishing costs. I also thank the Pyrotechnics Guild International, Inc., for their own generous grants toward completing our work.

Dr. Hardt left extensive instructions about how he wanted the book to appear as a published work. Essentially he wished that it follow the pattern of Ellern's organization in his last work but he wanted the information to be up-to-date and current. In the case of Ellern's book a guest author, the Rev'd. Ronald Lancaster, was asked to write the chapter on fireworks. Following this precedent, the gifted fireworks craftsman Barry Bush was willing to write the fireworks chapter for the present work. He also re-wrote and expanded the glossary. I also thank Dr. Jeremy Clayre for supplying information on Japanese firework techniques. Dr. Clayre worked at a Japanese fireworks factory during his student days.

Many technical advances have been made during the last decade of the past century, especially in the computer realm. Dr. Barry T. Neyer, Director of

Research and Development at PerkinElmer Optoelectronics, Miamisburg, Ohio, and also President of Neyer Software, Cincinnati, Ohio, generously agreed to write the chapter on statistical techniques, which covers the most recent progress in this area.

I should also like to thank the "team" who edited and updated the text. The editing team consisted of Barry Bush, Dr. Jeremy Clayre, Dr. Bernard E. Douda, Alex Schuman, and Michael S. Swisher.

Those familiar with the technical pyrotechnics literature will recognize Dr. Douda as the Senior Scientist for Pyrotechnics, Ordnance Engineering Directorate, NAVSEA Naval Surface Warfare Center at Crane, Indiana. Dr. Douda has been active in military pyrotechnics for fifty years. From more than a year of round-robin e-mail conferencing, I have a huge file of Bernie's suggestions, additions, and corrections, as well as a box of the reports and additional references he thought would be valuable in augmenting the original manuscript to reflect advances made in pyrotechnics since Dr. Hardt's death.

Dr. Clayre and Mr. Schuman made many a literature search and did much tedious bibliographical work. Mr. Schuman is employed by B/E Aerospace, Interior Systems Group, at Lenexa, Kansas.

Many thanks also go to the Rev'd. Ronald Lancaster, M.A., M.B.E., of Kimbolton Fireworks, Ltd. in England, who read the proof pages and offered many valuable suggestions and corrections.

Jorge Ferrando of Argentina, while managing Cienfuegos Ltda., a Brazilian fireworks factory using Chinese techniques, also generously allowed me to take photographs at their factory.

Most importantly, I extend my appreciation to Peggy Hardt Long, Dr. Hardt's widow, for her patience and encouragement over the many years.

ROBERT G. CARDWELL
Pyrotechnica Publications
September 2001

Author's Preface

Someone once said that "if two people share a responsibility, each one has about 10%." Whereas this book began as a revision of Herbert Ellern's first and second books, *Modern Pyrotechnics* (1961) and *Military and Civilian Pyrotechnics* (1968), the greatly expanded volume of recent primary references made a complete revision of the old material necessary.

Why another book on pyrotechnics? It has been almost 20 years since the last comprehensive review was published and a new look may serve to highlight these changes. This book is offered in the hope of meeting this objective at least in part by presenting an overview of the significant advances.

Instrumental analysis in the laboratory, electronic detection, and safety practices in the field have been improved. Production was affected by automation only to a small extent in processing of flare compositions. Micron-size metal powders are now routinely available for a reasonable price. Flash compositions have seen few advances. Low-voltage initiators are used with new primers and, in some applications, they have been supplanted by exploding bridgewires, laser initiators, and slapper-detonators.

Old applications have fallen into disfavor; new ones have come into being. Pyrotechnically actuated seat-belt cinchers, automobile airbags, and deflagrating energy-transfer systems are now used. Concern with environmental issues has brought about changes in the choice of organic dyes and in the protection of personnel handling them. Carcinogenic effects of chromates and the toxicity of certain firework ingredients have prompted the search for substitutes.

Yet the reader may be disappointed that many issues are not discussed more fully within the framework of the current state of the art. There is a corresponding need for a contemporary presentation of such subjects in new monographs. Subjects such as the instrumentation of radiometry in the visible and infrared spectral regions, as well as recent advances in exploding bridgewire and foil technologies need to be more fully explored. Image processing in the field (as in thermography) is now a reality and will aid in the development of improved applications for pyrotechnics. Even now the science of pyrotechnics offers much virgin territory for the study of high-temperature kinetics, spectroscopy, nonequilibrium thermodynamics, and numerical analysis.

I expect to see in the near future further development of new detonants based on metallic coördination compounds which are hot-wire sensitive yet stable and reasonably safe to handle. New energy-transfer systems will be perfected which depend on novel deflagrating compositions and on shock transmission. New solid state laser output will function either through fiberoptics or be generated *in situ.*

In the last twenty years the microcomputer has become the standard office and laboratory tool for the processing of large quantities of data as is required for Fourier transforms, in the calculation of equilibria, and in the study of kinetics. Compilations of available software and applications become obsolete almost as soon as they are published.

I have updated the material on the history and manufacture of the safety matches from the earlier books by Herbert Ellern, a subject of interest and value.

At times I would gladly have opted for a book written "by committee," especially because many disciplines, even within a narrowly defined branch of technology, require the expertise of a specialist. Still, so many individuals have given freely of their knowledge and advice that much of what is current is due to their help. Dr. Bernard Douda, Naval Surface Warfare Center, and Bob Blunt, formerly of the Denver Research Institute, were so kind as to read the manuscript in its entirety, and then to furnish what were in the end key references. To them I can only express my heartfelt gratitude. I thank Dr. Takeo Shimizu and the late Professor Shidlovskii for copies of their books, and I thank Dr. Shimizu for his gracious permission to use some of his material. I am also obliged to Dr. Stig Johansson of Intermatch Sweden AB for updating my material on matches. Special thanks go to the Lockheed Palo Alto Research Laboratory.

Dr. Ellern passed away since I began this book. I am fortunate to have been able to draw on his accumulated experience as contained in his earlier volumes. He had expressed the wish to see both the appearance of Halley's comet (for the second time) and the publication of my book, and I regret that he did neither.

ALEXANDER P. HARDT

Biographical Note

Alexander Paul Günter Hardt was born in Canton, China, on 16 June 1930. His grandfather, Paul Hardt, son of a veteran of the Franco-Prussian War and an artillery officer himself, married Hedwig Ringelmann, the only daughter of one of the oldest families in Osnabrück, Germany. Paul and Hedwig had two children, Helmut and Günter, Alex's father.

Günter, after several positions in Uruguay and Chile, found employment in Canton, where he met Doris Jane Marsales, a Michigan-born English instructor. They were married in December, 1929.

Alex, born the following year, was not a strong child, and five years later, with the threat of dysentery, malaria, and tuberculosis in China, his parents decided that Alex should live with his grandparents in Osnabrück where the climate was better and he could receive a healthier upbringing.

Alex, his mother, and his younger sister Joyce boarded a freighter at Madras, India. It was filled with wild animals bound for a zoo in Germany. Alex's mother and sister returned to China, and except for a six-month vacation during 1938, Alex would not see his parents again until 1947.

The young Alex lived in the Ringelmann house with his grandparents and received an excellent education in the German schools. These times, while not happy, were quite vivid in Alex's memory: the many schools he attended, and later the air raids, the firebombings, the destruction of the Ringelmann house, the War.

In March, 1947, at age 16, after much paperwork, Alex was on his way to America to rejoin his family in San Francisco. They had arrived there just before Pearl Harbor, and had rented an apartment. Alex's sister Joyce had made the acquaintance of Peggy Sorensen, whose parents lived nearby. The Hardt family moved later to Hillsborough but kept in touch with the Sorensens.

When Alex arrived in Hillsborough, he attended Burlingame High School to improve his English. Academically he was beyond the American high school curriculum. After graduating from Burlingame with honors, he enrolled at the University of California at Berkeley, where he was the first to pass all entrance exams on the first attempt. He studied chemistry there. His graduate studies were at the University of Washington at Seattle, and in four years Alex earned a Masters and Ph.D. degree in chemical engineering.

After graduation Alex worked for two years at Stauffer Chemical Company in Richmond, California, where he had worked during the summers as an undergraduate. He did not like this work and attended Boalt Hall Law School but soon tired of law. Eventually, in 1962, Hardt obtained employment at Lockheed Missiles and Space Co., Inc., at Palo Alto, California. There he worked extensively on tracer munitions, improving incendiary ignition systems, and exothermic intermetallic reactions, with emphasis on the chemical reactions of titanium and zirconium. He remained there until his terminal illness.

His publications, which touched, *inter alia,* upon tracers, intermetallics, self-propagating high temperature synthesis (SHS), and delays, were extensive, and some are cited in the present book[96-106, 189-190, 201]. Though he was primarily a contributor to journals and an author of government reports, he also was a significant contributor to the definitive *Encyclopedia of Explosives and Related Items*[72]. Among the monographs signed by him in that reference work are "Safety in the Energetic Materials Field" (pp. S6-S29); "Thermochemistry" (pp. T190-T204); "Ultrasonics in Ordnance" (pp. U26-U32); "Uranium" (pp. U85-U92); "Zinc" (pp. Z2-Z6); and "Zirconium and Hafnium" (pp. Z11-Z23). He also wrote the article on "Pyrotechnics" for the third (1982) edition of the Kirk/Othmer *Encyclopedia of Chemical Technology.*[129]

Hardt married Peggy Sorensen in June, 1960. In 1961 they purchased a house in Piedmont, California where two daughters were born: Janet Marie in 1963 and Jody Ann in 1965. The family soon afterward moved to Saratoga.

Alex worked extensively in the pyrotechnic field at Lockheed as a chemical engineer. During his employment there he became a good friend of Dr. Herbert Ellern and also of Dr. Takeo Shimizu, who also specialized in pyrotechnics, in the broader sense of that word as it applies to military and industrial applications.

This "big three" in the pyrotechnic field met together in 1985. Hardt and Shimizu were both active in the early days of the International Pyrotechnic Society (IPS).

Dr. Ellern's final book, *Military and Civilian Pyrotechnics,* was by then nearly twenty years old and out of print, and a revised and updated adaptation of the work was discussed extensively between Ellern and Hardt. Dr. Hardt began work on this new book in the mid-1980s, and the work was progressing towards completion when he was diagnosed with cancer early in 1989. He had just finished the first typescript some weeks before his untimely death on 21 April, 1989.

A Tribute to the Memory of Dr. Alexander P. Hardt

[from PYROTECHNICA • XIII (August, 1990)]

Dr. Alex Hardt looked quite tough as if he were one of the grand Muir redwoods in Mill Valley, California, which no wind or storm could blow down. He spoke very cheerfully when we were sitting around a dinner table in a restaurant with Mr. James L. Austing and his family. It was a pleasant evening at the 13th International Pyrotechnics Seminar in Grand Junction, Colorado, on 11-15 July, 1988.

Then, to my great surprise, I received a letter from Dr. Hardt dated 16 February, 1989, in which he wrote: "Shortly before Christmas, I was found to have inoperable cancer. I want to assure you of my appreciation of having known you and regret not to be able to host you at the 1990 meeting of the Franklin Society in San Francisco." It was the last letter to me from him. Thereafter, from Mr. Robert G. Cardwell's information, I knew his condition very rapidly became worse and he died on 21 April 1989. Mr. Cardwell enclosed a copy of the funeral service announcement in which there was a poem that could serve as Dr. Hardt's last will and testament:

> Please don't remember me with fears and sadness,
> Remember me with joy and laughter.
> For that's the way I'll remember you.

I saw Alex Hardt for the first time when I was in San Francisco in 1980 during my trip to the USA and Europe. He took me to Dr. Herbert Ellern's home, where we were warmly received for dinner by Dr. Ellern and his wife. I remember Dr. Ellern's very nice handmade cake that was presented to us. After the visit, Dr. Hardt took me to Mill Valley to see the Muir redwoods.

The second time I saw Dr. Hardt was in 1985, in Karlsruhe, W. Germany, on the occasion of the 10th International Pyrotechnics Seminar. He had a very thick manuscript of his book on pyrotechnics under his arm and asked me to read through it in one night. This perplexed me because I did not have enough time to read through it and only quickly went through the pages, returning it to him the next morning.

The third opportunity I had to see Dr. Hardt was in Vail, Colorado at the 11th IPS Seminar. He had a heavy copy of the seminar proceedings under his arm; he looked a man of sturdy physique.

We have recently lost two famous pyrotechnists of great erudition, Dr. Ellern on 17 March 1987 and now Dr. Alex Hardt, the successor of Dr. Ellern, just two years later, at the age of 59. A copy of the manuscript for his book is now on my worktable and I am reading it again at the request of Mr. Robert G. Cardwell (Dr. Hardt changed publishers shortly before his death, turning over the manuscript to Pyrotechnica Publications, to be published posthumously). I know it will not be an easy task to publish such a special work on pyrotechnics, and I hope to write some book reviews on it for journals on explosives in Japan which have many readers in English.

My thoughts and feelings go out to his surviving family: his wife, Peggy Hardt, and his two daughters, Janet and Jody, and his mother Doris Jane, who are, to my regret, unknown to me. I hope that people will warmly and kindly encourage them in the future days.

TAKEO SHIMIZU
Kawagoe-shi, Japan

Alexander P. Hardt, 1930-1989

[from the Saratoga, California *News*, 3 May, 1989]

A memorial service was held April 25 at St. Andrew's Episcopal Church for Alexander Hardt, who died on Apr. 21, 1989 in his home of cancer.

Born on June 16, 1930 in Canton, China, Hardt was raised in Germany where he went to school until the age of 17 [*sic*]. He came to the United States after World War II. A graduate of University of California, Berkeley, Hardt also had a Ph.D. in chemical engineering from the University of Washington, Seattle, Washington. He has lived in Saratoga for 24 years.

Hardt was employed as staff scientist at Lockheed Palo Alto Research Laboratory from 1962 until his retirement in January 1989. He has written numerous publications in scientific literature and has co-authored a book, *Military and Civilian Pyrotechnics* [*sic*]. A member of the International Pyrotechnics Society, he also liked to refinish antique furniture.

Hardt is survived by his wife Peggy Hardt of Saratoga, two daughters Janet Hardt Brocato of Vallejo, Jody Ann Hardt of San Leandro; son-in-law Mike Brocato; mother, Doris Jane Hardt of San Jose, and uncle Helmut Hardt of Germany.

The family requests contributions to be made to the Hospice of the Valley, 1150 S. Bascom Ave., San Jose, CA 95128.

About the Contributors

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Chapter 1

Definitions, Scope and Literature

Pyrotechnics is distinguished from the closely related technology of explosives and propellants though their functions frequently overlap. Because a large body of specific scientific knowledge has grown up for both, it would be quite wrong to include much of it in an introductory volume on pyrotechnics. Furthermore, pyrotechnics embodies many aspects of current advanced science which have never been treated systematically, and therefore the addition of one more book to the existing literature seems justified.

In general (though not exclusively) pyrotechnic reactions do not involve combustion with ambient material such as air or water because they usually proceed from the self-contained exothermic reactions of solid mixtures. These reactions can occur with or without the formation of gaseous products and at rates which can vary from moderate to explosive. Pyrotechnic reactions can be employed for the sake of the evolved heat, sound, smoke, light, flame, colored light, or gas. Pyrotechnic devices tend to be storable, portable, and capable of being triggered by a small external energy source. Moreover, they store energy more efficiently and cheaply than electrical or mechanical devices.

In the past it was customary to decry the primitive state of the science of pyrotechnics. Happily the last two decades have seen much improvement both in scope and content of published information.

Much of the literature on pyrotechnics has been published abroad, many of the older references being in German or Russian. One such is *Principles of Pyrotechnics* (Основы Пиротехники) by Professor A. A. Shidlovskii, which appeared in several editions in 1943, 1954, 1964 and 1973, and which has been translated into English as a Government report[214].

Herbert Ellern published *Modern Pyrotechnics*[69] in 1961 and *Military and Civilian Pyrotechnics*[70] in 1968. Ellern's work satisfied a critical need for an introduction to the subject. Both books emphasize an empirical approach with minimum stress on theory and analysis. At the same time, an attempt was made to avoid the format of a cookbook, by discussing underlying principles. Both books are now out of print,* prompting in part the undertaking of this work, intended as a successor.

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* *Military and Civilian Pyrotechnics* has recently been reprinted by its original publishers.

Pyrotechnic literature is commonly characterized by fragmentation and the lack of a comprehensive outlook. This is probably a reflection of the particular bias and background of the authors. Both Shidlovskii and Ellern have reviewed much of the early material. Because their references are generally not available, or are of an obscure nature, an attempt was made in the present work to rely on sources with a reasonably wide circulation.

The *Aerospace Ordnance Handbook*[192] contains useful information on pyrotechnic devices and is not restricted to a discussion of space applications. On the other hand, the first edition of *Handbook of Pyrotechnics*[25] by Karl O. Brauer, its title notwithstanding, encompasses aspects of ordnance initiation, as they apply to space technology.

Two more recent books are Joseph McLain's *Pyrotechnics*[161] which includes certain aspects of solid state chemistry, such as thermal analysis techniques, in an attempt to lay a scientific foundation for pyrotechnics. This trend of applying a more rigorous or analytical viewpoint was continued by John A. Conkling in his recent *The Chemistry of Pyrotechnics*[39].

The continuing fascination with fireworks is reflected in a steady supply of new references. Articles by Conkling[38] and Menke[165] have afforded brief overviews. A series of scholarly essays, published in irregular intervals, is edited by Robert G. Cardwell under the apt title PYROTECHNICA – OCCASIONAL PAPERS IN PYROTECHNICS[194]. These are superior references that can only be faulted in that to date, the subjects covered remain incomplete. They do, however, provide an anthology the expansion of which is anticipated.

Readers of fireworks literature are often exposed to shoddy publishing standards. It is therefore gratifying to find in Shimizu's works a willingness to present information which has been traditionally regarded as a closely held secret. Only the description of fireworks manufacture can adequately illustrate the division between fireworks and military pyrotechnics with its emphasis on reliability and industrial producibility. Civilian fireworks manufacture retains much of the character of a cottage industry. Shimizu's *Fireworks, the Art Science and Technique*[216] is an updated English version of an earlier Japanese publication. It is particularly useful as a reference on the selection of pyrotechnic ingredients and for its graphic description of some techniques in the actual assembly of devices. A recent translation of Shimizu's *Fireworks from a Physical Standpoint*[215] is also an important effort to treat firework phenomena in a systematic and rational manner.

Relatively current (1998) is Ronald Lancaster's *Fireworks Principles and Practice* (third edition).[139] First published in 1972, this book is considered the standard authoritative work on fireworks. The earlier *Chemistry of Powder and Explosives* by T. L. Davis[44] was a classic reference, so much so in fact, that it has been described as the "case of the missing pyrotechnics book" owing to the tendency of being "borrowed" without permission from public and private collections. It contains a substantial formulary, much of it dated, but is copiously illustrated with quaint half-tones and drawings. Having been out of print for many years, it was recently republished on the expiration of the original copyright. Davis's book illustrates the risk of fulfilling the expectations of the amateur fireworks enthusiast, to the extent that public libraries are loath to buy the book owing to the danger to public property and lives as well as the tendency for its ownership to be brief.

Weingart's manual, *Pyrotechnics*[249], though in many respects badly outdated, remains in print and is also regarded as a classic reference on fireworks. The last edition, dated 1947, is in fact a revision of a series of works, the first of which appeared in 1930. While not reflective of the current state of firework manufacture, the book contains much information about techniques and effects that is not to be found elsewhere, and for this reason it deserves mention.

George Plimpton's coffee table book *Fireworks: A History and Celebration*[191], is copiously illustrated, and of great interest to those wishing to explore the ethnic roots of fireworks in America. A relatively recent German contribution is *Das Buch der Feuerwerkskunst*, Greno Verlag, 1987 (G. Sievernich, Ed.) which is larger and more costly than Plimpton's and quite devoid of technical information.

Great emphasis on the historical and martial aspects of pyrotechnics is found in Partington's *History of Greek Fire and Gunpowder*[182]. The original edition, long out of print, has become a collector's item, and recently a reprint has been issued. Good reviews are sometimes found in technical encyclopedias, although one has to seek information under more than one entry. Ellern and this author provided, for instance, the material for "Matches" and "Pyrotechnics," respectively, for the current issue of Kirk-Othmer's *Encyclopedia of Chemical Technology*[129], as did Johansson elsewhere[123]. General encyclopedias may be strong on the historical aspects of match manufacture, but weak on technical details about any topics in pyrotechnics. Matches have also been treated in a recent monograph[78] which is recommended to the reader who wishes to go beyond the material presented in Chapter 11 of this book.

Military pyrotechnics have been explored rather thoroughly in the *Encyclopedia of Explosives and Related Items*[72], published over a period of 20 years as a set of ten volumes. One is told that this effort will be the last one for the publication of hard copies, and that in the future the material will be published in a computer-accessible form. The reader is cautioned when using this reference in that more recent information is found under the last letters of the alphabet: *azides* are discussed under "p" for *primary explosives* and *ignition mixtures* can be found under "z" for *zirconium mixtures*. The index at the end of Volume 10 provides useful cross-referencing assistance.

Information on military pyrotechnics is well presented in the *Military Pyrotechnics* series[169-171] which, though dated, covers the subject more thoroughly than do technical reports that are generated by the various laboratories of the armed services. Moreover, reports and other publications issued by the U.S. government are available through the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield VA 22161, identified by an "AD number". The mere existence of an "AD number" is, of course, no assurance that the report is still in print. As with other sources in the pyrotechnics literature, many of the older citations are much sought after and may have to be obtained as a photocopy. Some reports have a limited (restricted) distribution, even if they are not classified.

In recent years, scientific journals have provided a platform for the discussion of current advances. The PROCEEDINGS of the biannual meetings of the International Pyrotechnics Seminar (formerly sponsored by the Denver Research Institute, but now by the Illinois Institute of Technology), have been published in bound volumes which may be back-ordered. The Franklin Research Laboratories, Philadelphia, Pennsylvania, have also sponsored biannual Symposia on Explosives and Pyrotechnics the PROCEEDINGS of which have also been published. The recently formed International Pyrotechnics Society publishes PROPELLANTS, EXPLOSIVES AND PYROTECHNICS (successor to EXPLOSIVSTOFFE) for the multilingual community. Searches of COMBUSTION AND FLAME, of the PROCEEDINGS OF THE COMBUSTION INSTITUTE and of the Russian PHYSICS OF COMBUSTION AND EXPLOSION are also frequently rewarding.

In his books, Herbert Ellern also provided citations on military specifications of the devices and components described. It is the experience of this author that without exception, the specification is outdated or superseded. For this reason such information has been mostly omitted in this book, but if the reader desires the current data, he is directed to the Department of Defense *Index of Specifications and Standards*.

Finally, those interested in an exhaustive listing of older books on fireworks may refer to *A Bibliography of Fireworks Books*[188] by Chris Philip. While bibliographies of works of pyrotechnic interest have often been appended to books about other aspects of pyrotechnics, this outstanding and extensive bibliography is the only one on this subject to stand on its own.

Chapter 2

Safety and Handling of Hazardous Materials

Safety problems arise partly because concerns in pyrotechnics differ from those encountered with explosives and propellants. Pyrotechnic devices contain complex mixtures, the hazardous properties of which depend on many factors. Hazards derive from electrostatic sensitivity, particle size, stoichiometry, and chemical potential, to mention a few factors. Sensitivity to initiation can be affected by heat, shock, friction, and moisture. Propellants and explosives, on the other hand, are usually either single compounds, or mixtures the hazardous properties of which are primarily determined by the explosive constituent.

The number of accidents per capita employed in the pyrotechnic industry (particularly in the civilian sector) is much larger than in related industries. Tragic occurrences in school chemistry laboratories are sufficient reason to classify these events by type and to establish guidelines for their prevention.

The principal hazard in pyrotechnics is, of course, uncontrolled ignition followed by combustion in confined spaces. Pyrotechnic mixtures contain their own oxidizers and will burn without air, although sometimes not to completion. Frequently explosions are described as being detonations. Properly speaking, detonations result from high-order (complex kinetic) decomposition of an explosive, and produce reaction fronts which propagate at supersonic speeds as a "shock wave." Such shock waves expand radially from the source and can be confined (to some extent) with barricades. By contrast, barricades tend to confine and channel an explosion so that the debris and flame is directed with particular danger to structures and personnel. Death and injury from pyrotechnic accidents are caused by burns, fragment impact, and lung damage. Each instance of pyrotechnic handling must be examined separately with respect to:

- the quantity of reactive materials
- the manner of confinement
- shielding against the spread of fire and the scattering of fragments
- sources of initiation

One of the most hazardous aspects of handling pyrotechnic materials derives from the difficulty of predicting the initiation sensitivity of new combinations of familiar ingredients. Of course, preliminary conclusions can be drawn from the combustion rate and ignition temperature. Preliminary tests therefore tend to include igniting a gram-size quantity. Unfortunately, all such tests produce mere warning signs because a seemingly safe result does not preclude hazardous consequences if the mixture should be confined, moist, dry, or otherwise different in some small measure from the test sample.

This uncertainty leads to the practical rule that every pyrotechnic operation should be considered potentially dangerous even if initial safety tests aimed at preventing accidental initiation have been reassuring. Therefore, the emphasis lies on the ever-present and undeniable possibility of accidental initiation, rather than on the means of reducing the chances of mishap. This helps change the attitude from one of complacency ("Everything has been done to prevent an accident") to the more realistic view anticipating a "worst case" scenario (*i.e.*, "what happens if the mixture goes off notwithstanding all measures taken?").

Because complete remote control of weighing, mixing and processing in the workplace is not feasible on the floor, protection of personnel is a matter of primary importance. In the laboratory this means handling gram-size quantities, protecting the eyes, face, and hands, and preventing the ignition of clothing. While taking these measures, compromises are necessary in order to make the worker accept the encumbrances of safety glasses, gloves, safety shields, etc., and also not to hinder the operator in fulfilling his task adequately. The idea that an operator will protect himself out of self-interest is unfortunately incorrect. Because of such unwillingness to obey mere exhortations, absolute rules must be given to the worker to wear safety equipment. Usually, there are no difficulties with those who already wear eyeglasses. But the person who does not wear glasses away from work (or who wears contact lenses) must be required to wear eye protection in the work area at all times and may not be permitted to use his own judgment in this matter. Even if the worker (*e.g.*, a janitor) merely handles an inert material, that worker may be near a co-worker engaged in hazardous operations. Side-shields on eyeglasses or goggles are a desirable protection, but are often mistakenly forgone in order to make the lesser protection of ordinary safety glasses acceptable and enforceable. Another important safety measure falls into the category of housekeeping in that no flammable liquids or energetic substances may be stored near the worker, as fires could spread much faster than if the work substance alone were involved.

When handling priming mixtures, first-fires and the like, even in small quantities, the use of a stationary shield made of reinforced glass, or a polycarbonate such as "Lexan," with access ports for the gloved and grounded hands, is strongly recommended.

Suede leather gloves (which are washable but which must be kept clean*) permit mobility of the fingers while affording protection against searing flashes. Rubber or plastic gloves must never be worn because they can melt when hot and stick to damaged skin, making their use worse than no protection at all.

Many mixtures, particularly those compounded without metallic ingredients, and which may contain a primary explosive, are so sensitive to static discharge as to be susceptible to initiation by the accumulated charge on the body of a worker who is improperly grounded or clothed. In very cold climates and in very arid climates, these risks are particularly severe. As a matter of routine, the work area should be covered with a grounded conductor and the operator should be grounded with wrist-straps. As a further precaution, pyrotechnic mixtures should be stored in nonsparking metal cans or other conductive containers.

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* They are easily washed in lukewarm water while on the hands. When clean, a rinse after the final soaping is omitted. This keeps the gloves flexible after drying.

In outer clothing, anything that is reasonably flame-resistant and does not lend itself to build-up of static charges is permissible. Wool clothing, although it does create static charges, is an excellent protective covering. Nylon garments should be avoided because of poor protection against flash fires (they melt) and because of the pronounced tendency to accumulate static charges. Many garments recommended for pyrotechnic work have proven to be hazardous in themselves in that they induce clumsiness or are so uncomfortable that they tempt the operators to remove them. Cotton clothes have the advantage of being insignificant generators of static charges, but unless fireproofed, are easily ignited. This is particularly the case once clothing has become impregnated with pyrotechnic materials. Regular laundering of all work clothes is recommended. Safety showers are most desirable, while safety blankets are of dubious value.

There is a difference between hazards to be avoided in the laboratory and those encountered in the production of pyrotechnic devices on an industrial scale.[11] Production facilities may have remote-controlled operations and specially designed equipment protecting operators from mishaps. On the other hand, the quantity of materials being handled in such situations is so much greater that procedures acceptable on a laboratory scale are no longer so in a production scale.

One of the variables to be controlled is relative humidity, which has a strong effect on the moisture content and hence, the electrical resistance of the mixtures. Low moisture content increases the likelihood of a static charge. This problem is further complicated by the presence of complex mixtures of fuels and oxidizers, each with its own peculiar response to external stimuli.

Many authorities caution against the use of oscillatory granulators and the hand screening of chlorate and perchlorate mixtures containing metals. Shidlovskii[214] warns against the mixing of zinc, aluminum, or magnesium with heavy-metal salts, especially if the latter are hygroscopic. To do so may bring about double decomposition reactions which could lead to instability in the mixtures. The charging of lead azide into copper receptacles, for example, may result in formation of highly unstable cupric azide. Another hazardous exchange reaction may occur when chlorates are mixed with ammonium salts, leading to the possible formation of ammonium chlorate, which is prone to spontaneous decomposition.

The Problem of Hazardous Chemicals

In general, pyrotechnic ingredients themselves tend to be safe, aside from the problem of toxicity. But whenever an oxidizer contacts a reducing material, a reaction is possible. By its very nature there can be no such thing as a "safe" pyrotechnic mixture. Contact between pyrotechnic mixtures and reactive materials can be inadvertent, as through the dispersion of a combustible dust in air, wetting with water, or the use of a carbonaceous additive to oxidizers as an anti-caking agent.*

Reactive metals reduce chlorinated hydrocarbons; as an extreme example, a dispersion of metallic sodium in carbon tetrachloride has explosive properties. Chlorinated hydrocarbons may be excellent degreasing agents, but they must never be used in place of hydrocarbon solvents.

Whereas some oxidizers can explode by themselves (*e.g.*, ammonium perchlorate, ammonium nitrate) the principal danger arises from their admixture with fuels. Mixtures of chlorates with carbonaceous fuels are more dangerous than some mixtures with metallic fuels, because on reaction, gaseous products are formed which produce large propagation velocities in confined spaces. While these propagation velocities may reach 2000 m/s (as can black powder explosions), the propagation rates are below the sound velocity in that medium and therefore have more the characteristics of an explosion than of a detonation. Ammonium perchlorate can explode violently, as it does in flash compositions containing 35-40% aluminum powder. This reaction produces a greater gas volume than does the same mass of nitroglycerine.

Pyrotechnic reactions take place upon the dissociation of the oxidizer, a process which generally requires the input of heat. Chlorates decompose exothermically with almost zero heat of activation; a chlorate reaction, once initiated, propagates more rapidly than would be the case, *cæteris paribus*, with another oxidizer. This exothermicity of chlorate decomposition also greatly facilitates the ignition process. Blends of potassium chlorate with aluminum or with antimony sulfide are capable of violent explosion in small quantities, and can thus be used as the exploding charge in firecrackers.

A peculiar problem has been reported in the European pyrotechnics literature[237]. The availability of sodium chlorate as a weed killer has prompted its use, when mixed with sugar, as a bomb explosive. Sodium chloride has been found to desensitize the chlorate, but such phlegmatization should not be considered a solution to the problems posed by making chlorates available to the general public without control.

No mixture of a chlorate with sulfur should be prepared, wet or dry, unless a carbonate or bicarbonate is added as an inhibitor before mixing. Even more dangerous is the mixture contained in toy caps† ("amorces") which is prepared from a wet slurry of red phosphorus and potassium chlorate with calcium carbonate as the inhibitor. This combination is the most sensitive and unpredictable of contemporary pyrotechnic mixtures, and its preparation should never be attempted by amateurs. Similarly, high school chemistry classes should never have access to a chlorate and red phosphorus at the same time.

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* The Texas City explosion of 1947 was the result of a 1% wax coating on fertilizer grade ammonium nitrate in paper bags. The wax acted as a sensitizer, causing progression from deflagration to detonation. The combination of ammonium nitrate and paper was shown to be self-heating during bagging and shipping, causing spontaneous fires in transit. The wax coating has since been replaced with diatomaceous earth[40].

† Caps or toy "torpedoes" should never be stored in the same magazine or shipped in the same shipment with other fireworks. Explosion of one is certain to explode others in the same package.

Noisy reports, for amusement or demonstrations, may be produced from nitrogen triiodide, which is prepared by the addition of ammonia water to iodine crystals. When the product is allowed to dry, it becomes so sensitive to initiation that it cannot be moved or touched, and it cannot be stored in the dry state.

In handling fuels, it should be remembered that finely divided material can cause dust explosions. The particular hazards inherent in the handling of pyrophoric phosphorus, zirconium, and similar materials are examined individually in separate chapters. Here it suffices to note that safety instructions on labels should be strictly followed. For instance, if shipment is made in metal cans, the contents should not be transferred to glass jars. If the shipment is made dry, water should not be added except with special precautions (see below). If samples are shipped wet, they should be dried under an inert atmosphere.

Water may be, only with due caution, used to blend mixtures containing zinc, aluminum or magnesium (see below); likewise it should not be used with fine titanium or zirconium powders unless in a volume ratio of at least 20 to 1. Wet slurries, formed by settled zirconium, are particularly hazardous if they are removed from the container without excess water.

Nitrate mixtures tend to be relatively stable, as compared with chlorate mixtures, because of the high heat of dissociation. Ammonium nitrate is sensitized by carbonaceous materials and also by metal powders, especially Al-Mg (magnalium) alloy. Metal powders, in combination with water, may have explosive properties when initiated by a detonator. Moisture can cause the corrosion of metal powders, and the hydrogen formed by this reaction can reduce nitrates to ammonium salts. Thus, moist barium nitrate reacts with magnesium forming magnesium hydroxide and ammonia, resulting in an alkaline environment which slows further corrosion of the magnesium. The reaction of water with magnesium is accelerated in an acid medium and is inhibited in a basic medium whereas the behavior of aluminum (which is amphoteric) in practice reacts in the opposite way. Consequently, moist sodium nitrate reacts with aluminum to form weakly basic sodium aluminate. Therefore, sodium nitrate-aluminum flare compositions are unstable on storage unless sealed against moisture. The less hygroscopic the salt, the more stable the composition. All mixtures, except those with alkali metal nitrates, are more stable with aluminum than with magnesium. The addition of sulfur to a mixture increases its acidity, so that mixtures containing both sulfur and magnesium are less stable than those without sulfur. Likewise, magnesium reduces cupric nitrate or lead nitrate to form the respective element and hygroscopic magnesium nitrate. This reaction is even more dramatic with silver nitrate: a mixture of finely ground magnesium with silver nitrate reacts with a flash upon the addition of a drop of water. Barium peroxide, a weak base, is more stable with magnesium than with aluminum, explaining the use of barium peroxide in ignition compositions. Ammonium salts of strong acids corrode magnesium more than aluminum. Therefore, aluminum is used in propellants containing ammonium perchlorate or ammonium nitrate.

Toxicity Hazards

Some constituents of pyrotechnic compositions are toxic. Curiously, this matter has never been treated in a comprehensive manner with respect to pyrotechnics and such information as exists is buried in governments reports dealing with specific devices[51, 96] or within references to toxicology[3]. Certain materials have been reported to be carcinogenic, while others cause respiratory problems or allergies. Some toxic agents act in an acute manner, causing little lasting harm while others are cumulative and can bring about chronic damage. With toxic pyrotechnic compositions, rules of good housekeeping go far to minimize potential health risks. However, the tendency to accumulate large quantities of waste materials during manufacture and the need to store a large inventory of finished devices present disposal problems which have only been addressed in recent years to the extent mandated by environmental regulations. This matter is examined in more detail in the next chapter.

Toxicology is replete with its own terminology and conventions of which only three are defined here:

TLV- TWA Threshold Limit Value – Time Weighted Average

The time-weighted average concentration for a normal 8-hour work day and a 40-hour work week to which most workers may be safely exposed day after day without adverse effect.

TLV-STEL Threshold Limit Value – Short Term Exposure Limit

The concentration to which workers can be exposed continuously for a short period without suffering irritation, chronic or irreversible tissue damage, or narcosis of sufficient degree as to increase the likelihood of accidental injury, impair self-rescue, or materially reduce work efficiency. STEL exposure should last no longer than 15 minutes and should not be repeated more than four times a day.

TLV-C Threshold Limit Value – Ceiling

The concentration that should not be exceeded even briefly. Concentrations are usually expressed as part per million (ppm) for gases, *i.e.*, volume % times 10^4, or mass per unit volume, mg/m^3, for solids. The last term, together with the bulk density and particle size, defines the particle count per unit volume. The data listed in Table 2-1 are by no means comprehensive, but deal only with substances of obvious interest to pyrotechnists. Many of the derivatives are equally toxic but because they may be uncommon in pyrotechnics, have not been included.

Carcinogens

Materials identified as carcinogens have either proven carcinogenic in man, or have induced cancer in animals under experimental conditions. For many of the organic dyes, no TLVs have been assigned. Cigarette smoking can enhance the incidence of respiratory cancers from these substances. Only those substances shown to be carcinogenic at doses below one mg/m^3 have been listed when the evidence was derived from respiratory, dermal, or gastrointestinal tests[3]. Others are listed by Vigus and Deiner[243] and by Cichowicz[33]. More material on colored smoke compositions and their toxicology is presented in Chapter 20. The following dyes or derivatives of dyes found in colored smokes are listed as carcinogens:

2-naphthol (β-naphthol)
2-naphthylamine
2-, 4-, 8-, 9-dibenzopyrene, an impurity in Indanthrene Golden Yellow GK
1-methylaminoanthraquinone (red dye)
1-phenylazo β-naphthol (Sudan Orange R)
1-(2 methoxyphenylazo)-2-naphthol
2-quinolyl-2-indandione-1-, 3 (Rhodamine B)
1-(4-*o*-tolylazo-*o*-tolylazo)-β-naphthol (Sudan IV)
1-xylylazo-2-naphthol
2-, 5-dimethoxyphenylazo-2-naphthol (Citrus Red #2)
1-, 4-diamino-2-, 3- dihydroanthraquinone

Table 2-1. Toxicity Guidelines for Pyrotechnics[183]

Substance	**TWA**		**STEL**		**Concern**
	ppm	mg/m^3	ppm	mg/m^3	
Antimony and its compounds, as Sb	-	0.5	-	-	Possible Carcinogen
Arsenic and its compounds, as As	-	0.2	-	-	Carcinogen
Arsine	0.5	0.2	-	-	
Barium compounds as Ba	-	0.5	-	-	
Biphenyl					
as a constituent in dyes	0.2	1.5	0.6	4	
when chlorinated	-	0.5	-	2	
Cadmium, dust or salts as Cd	-	0.05	-	0.2	
Camphor, synthetic	2	12	3	18	Irritant
Chromium, metal	-	0.5	-	-	
Cr (III)	-	0.05	-	-	Carcinogen
Cr (VI)	-	0.05	-	-	Carcinogen
Decaborane	0.05	0.3	0.15	0.9	
Hydroquinone as constituent in dye	-	2	-	4	
Iron, carbonyl	0.1	0.8	0.2	1.6	
Lead, fume or dust					
as Pb	-	0.15	-	0.45	Neurotoxic
as chromate	-	0.05	-	-	Carcinogen
Mercury, compounds	-	0.1	-	-	
Nickel, carbonyl	0.05	0.35	-	-	
Phosphorus, yellow	-	0.1	-	-	Tooth & Bone Damage
Phosphine	0.3	0.4	1	1	
Phosphorus oxychloride	0.1	0.6	0.5	3	
Uranium, compounds	-	0.2	-	0.6	
Zinc chloride, fume	-	1	-	2	
Zinc chromate	-	0.05	-	-	Carcinogen
Zinc oxide, fume	-	5	-	10	

Chapter 3

Disposal of Hazardous Materials

The quantities of hazardous pyrotechnic materials stored are enormous, in some cases on the order of hundreds of tons. The least expensive disposal method has been incineration by open burning. In many places, this procedure is no longer permissible. An elaborate technology for incineration in furnaces with monitoring of the waste products has been developed.[53, 153] Incineration is the only disposal method available which addresses the diverse problems posed by waste. For instance, aromatic hydrocarbons, such as many dyes, explosives and binders, are highly stable chemicals which are toxic if allowed to escape from underground storage, outdated munitions, drums, tanks or other containers. Horror stories of toxic effects from contaminated drinking water or atmospheres in contaminated structures have caused the courts to make careless handling of potential toxins a costly experience for both private and government facilities. It is for this reason that as part of the release procedure for new munitions, plants and facilities for the demilitarization of munitions must be provided.

Demilitarization must be tailored for each hazardous component. Laboratory techniques, such as treatment with alcoholic potassium hydroxide, are not effective because they do not address the disposal of the reaction products which may contain oxidizers and heavy metals. Currently such problems are turned over to disposal companies which tend to put the materials into drums and forget about them. Much pyrotechnic waste contains heavy metal compounds (lead, strontium, barium, zinc, mercury, chromium, cadmium, copper, antimony) which can be separated and reduced to ash. The cost of recovery, especially from dilute wash and rinse solutions, is high, and the cost of ultimate disposal would be smaller if the demilitarization were connected with a larger incineration facility. At present, ash is used as landfill where it is subject to leaching. Fusing of the ash after admixture with a silicate to stabilize the product has been tested but is not yet practiced on a large scale. Because this method is also suitable for the treatment of nuclear waste products, it deserves further attention.

Many components of pyrotechnic mixtures are costly (as well as toxic) and these can be recycled. Below are brief descriptions of such practices.

Demilitarization, the disassembly and disposal of munitions, is itself a costly operation. Each device is cut apart by remotely controlled, specially designed equipment. The sectioned components are processed in dedicated facilities. For example, a typical photoflash cartridge containing an unconsolidated (loose) mixture of aluminum powder, potassium perchlorate and barium nitrate is cut and then the contents are extracted with 55° C water. The black powder expelling charge is processed separately. The suspended aluminum powder is removed by filtration. The solution is cooled to 20° C, causing the salts to precipitate, and these are recovered as solids. The saturated liquid is returned to the processor for reheating. Both the aluminum and the salt mixture are dried and recycled to the plant as raw material for production of new photoflash cartridges.[222]

Red phosphorus-containing mixtures are burned in a closed incinerator. The phosphorus pentoxide is scrubbed from the gas stream, and the resulting phosphoric acid is sold as fertilizer.[173]

Some photoflash mixtures consist of magnesium and sodium nitrate. In such cases the nitrate can be leached and sold as dilute fertilizer in areas where sufficient rainfall assures that the sodium build-up in the soil is minimized. The magnesium powder is recycled.[221]

Plastic-bonded explosives and propellants have been demilitarized by cutting the propellant grain with high-pressure water jets and extracting the oxidizer for recycling. For instance, RDX and HMX have been so recovered, using alcohol.

Colored smoke mixtures are burned in two-stage, closed incinerators, the second stage being performed in an afterburner at temperatures above 800° C in order to remove aromatic components from the effluent.[6]

Incineration is the only method of disposal available for the destruction of very stable molecules. Much effort has been devoted to the disposal of polychlorinated biphenyls (PCBs), which share with some organic dyes, explosives, and pesticides the potential for great environmental harm. Environmentally acceptable disposal of aromatic hydrocarbons by combustion requires the consideration of several factors not usually encountered in chemical waste incineration. Highly stable molecules require high combustion temperatures and relatively long "residence times." Excess air or additional fuel may be required.

The combustion criteria stated are based on the particularly stringent regulations[7] for the disposal of PCBs. The regulations specify three different types of combustion efficiency, which together define the performance required. First, a combustion efficiency of 99.9%, based on the complete conversion of carbon to carbon dioxide, must be attained. This means that for a CO_2 level of 10% or greater, the CO level must be below 100 ppm. Second, the combustion efficiency should be 99.99% based on a comparison of the chlorinated hydrocarbon emission with the feed of aromatic hydrocarbons in the pyrotechnic mixture, and lastly, the air emission of aromatic hydrocarbons must be less than 0.0001 mg/kg of feed. This is equivalent to a 99.9999% destruction of volatile hydrocarbons.

The aromatic content in the residue is not directly specified, but it is desirable that it be reduced to 50 ppm.

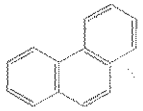
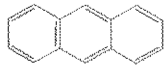
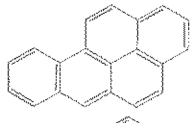
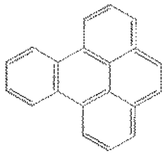
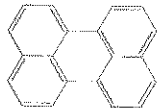
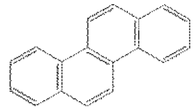
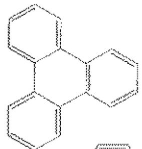
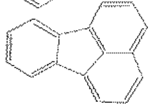
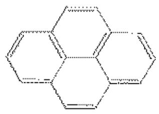
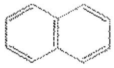
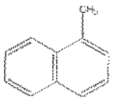
The following data are known for PCBs:

99.995% destruction at 1000° C and 1 second residence time.
99.999994% destruction at 2.0 – 2.9 seconds residence time, 10-70% excess oxygen residue
99.999% destruction at 1230° C, 2.3 seconds in afterburner, 80% excess air.

Thermal degradation of volatile toxins has been investigated in cement kilns, utility boilers, and sludge incinerators. EPA regulations specify temperature and residence time requirements much greater than those commonly encountered in most routine combustion operations. The incineration of aromatic hydrocarbons in an environmentally acceptable manner has been demonstrated in several of these devices and has been performed routinely at a number of commercial facilities. "The present difficulties lie not in technical performance areas, but in the political aspects of facility siting, testing, and approval."[6]

Incineration requires that effluents be monitored to assure destruction of the volatile toxins. Molecular fluorescence has been developed for this purpose[151] and the polynuclear aromatic hydrocarbons found are shown in Table 3.1. The technique permits real-time measurements for the detection of aromatic hydrocarbons in the 1 ppm range. Because the detection point is downstream of the venturi scrubber, the gas stream will be cold, and owing to the low vapor pressure of the polynuclear hydrocarbons, the reading of the volatiles level will be close to zero.

Table 3-1. Polynuclear Aromatic Hydrocarbons Found in the Combustion Product of Navy Colored Smoke Compositions.[151]

Compound	Formula	Structure
Phenanthrene	$C_{14}H_{10}$	
Anthracene	$C_{14}H_{10}$	
Benzo(a)pyrene	$C_{20}H_{12}$	
Benzo(e)pyrene	$C_{20}H_{12}$	
Perylene	$C_{20}H_{12}$	
Chrysene	$C_{18}H_{12}$	
Triphenylene	$C_{18}H_{12}$	
Fluoranthrene	$C_{16}H_{10}$	
Pyrene	$C_{16}H_{10}$	
Naphthalene	$C_{10}H_8$	
1-Methylnaphthalene	$C_{11}H_{10}$	

Chapter 4

Statistical Test and Analysis Methods[*]

Introduction

Even by following rigorous manufacturing procedures, it is impossible to make a group of identical pyrotechnic devices. Each one will have slightly different characteristics. There will be variations in the pyrotechnic powder, the density at which the powder is loaded, the geometry of the device, the coupling of the powder to the initiating mechanism, as well as variations in the initiating mechanism itself. There are also variations in the environments in which the device has been stored since the time the device was manufactured. Many of these variations will affect the performance of the device. A pyrotechnic device built to a good design will have minimal performance variation; however, some is inevitable.

Variation in device performance can be characterized as either initiation variation or output variation. Some examples of output variation are the function time, the pressure, the luminosity, etc. It is generally a simple matter to measure these variations. By measuring the various output characteristics of a sample of devices, one can estimate the output characteristics of the population as a whole by using standard statistical techniques. For example, the mean function time can be estimated by measuring the function time of a sample of devices and computing the arithmetic mean. Similarly, the variation of the population can be estimated by computing the standard deviation of the sample. Because measurement of a large number of devices is required to establish the probability distribution, the actual distribution is usually unknown and a normal distribution is assumed. Using standard statistical techniques it is straightforward to estimate the parameters of the populations as well as various confidence intervals for these estimates.

It is usually more difficult to characterize initiation variation. For most pyrotechnic devices, it is assumed that there is a critical stress level that is just sufficient to cause initiation. Any stress level below the critical value will not cause initiation, while any stress level above the critical stress will cause initiation. The form of the critical stress depends on the device. Examples include current in a bridgewire device, height from which a mass is dropped on the powder, or the gap which an initiating charge must overcome to initiate the donor charge.

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[*] This chapter has been written by Barry T. Neyer, Ph.D. Thanks are extended to John P. and Mary Jo Neyer, Cincinnati, and John O. Bennett, NSWC-Crane, for their suggestions and comments.

There are some techniques such as Electro Thermal Response[202] (ETR) and bridgewire resistance measurement that are often used to measure the "health" of the device (whether it will work). Some claim[172] that these techniques can be used to determine the critical stress of bridgewire devices, but this view is not commonly accepted. Unfortunately, there is generally no way to measure the critical stress of a device. The only measurement that can be performed is to monitor the response of a device to a given stress level. Moreover, it is also not generally possible to "home in" or "sneak up" on the critical stress level. If the critical stress is exceeded, the device will initiate, preventing any further testing. If the device does not initiate, it is usually modified by the stress. Thus, it is only possible to test any given device one time.

The only way that the initiation characteristics of a population of devices can be established is to select a sample of the devices, test each device at a given test level, and record the response (initiation) or lack of response. Unlike the case of output characteristics that can be measured, computation of the mean initiation stress is more difficult. One cannot compute the average of the individual devices because there is no way to determine the individual's critical stress. Nevertheless, using the more sophisticated techniques discussed in this chapter, it is possible to compute estimates of the population mean, standard deviation or other population statistics.

Obviously, if the test levels are chosen such that they are all far higher than the average critical stress levels of the population, not much is learned from the test. A similar result occurs for levels chosen far below the mean. Thus, unlike the measurement of output characteristics, great care must be utilized in the test design to select the test levels such that maximum information is obtained. Various test methods have been developed over the years that select the test levels in a manner that provides efficient estimation of the parameters of the population. These techniques are detailed later in this chapter.

The statistical test and analysis techniques discussed in this chapter are not limited to the field of pyrotechnics or energetic devices. Similar statistical techniques are also used to study the toxicology of various compounds, the ability of helmets to protect the head from injury, or the length of time that the brain can be without oxygen. The general name for this type of statistical test and analysis is sensitivity testing and analysis. The discussion in the following sections applies equally to these fields as well.

Estimates of μ and σ

The purpose of performing a sensitivity test is to estimate the parameters of the distribution. These estimates may be of the location and scale parameters, the mean μ and the standard deviation σ, or of various probability levels such as the stress that is sufficient to cause 99.9% of the items to respond. For most distributions, knowledge of the mean and standard deviation is sufficient to compute any required probability level.

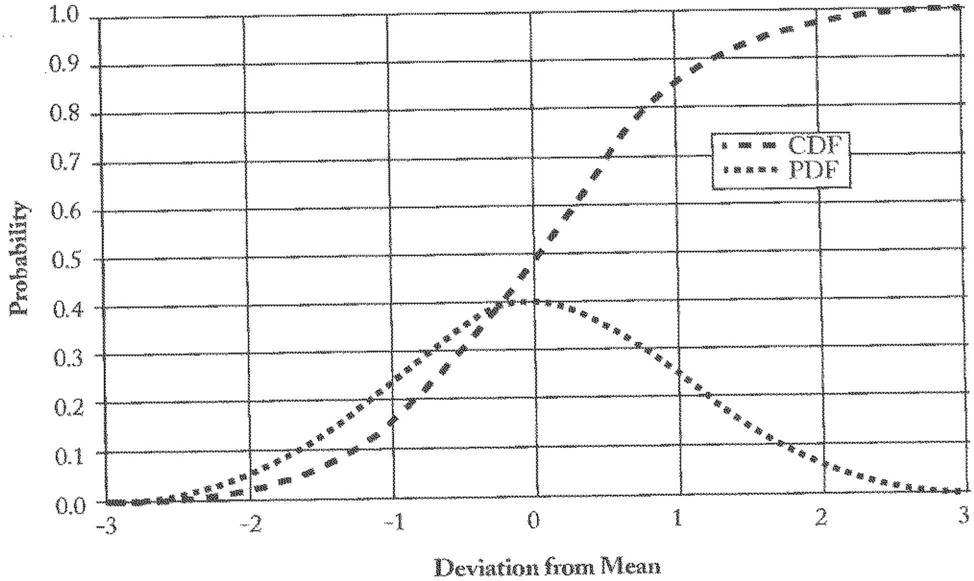

Figure 4-1. Normal probability functions.

The rest of this chapter assumes that the probability response function takes the form:

$$p = P[(x - \mu)/\sigma], \qquad \textbf{[4-1]}$$

where p is the probability of response, P is the probability function, x is the (transformed) stimulus level, and μ and σ are the location and scale parameters. The examples assume that P is a normal cumulative distribution function (CDF), such is shown in Fig. 4-1. The CDF, zero at small values and one at large values, gives the probability that an item chosen at random from a sample has a characteristic less than or equal to a given value. The probability density function (PDF) is also shown in Fig. 4-1. The integral of the PDF over an interval gives the probability that the characteristic is within the interval. The CDF is the integral of the PDF. If the probability function is not normal, then often a suitable transformation of the stress levels will make the distribution normal. (For many fields x is the log of the applied stress.) The exact form of the distribution curve will be stated where it makes a difference to the discussion.

The purpose of statistical analysis is to compute the parameters of the population that are accurate and precise. Accurate means that the parameters give the true value on the average, that is, there is no bias. Precise means that the variation in the estimates of the parameters is as small as possible. There is always some statistical variation in any estimate of the parameters. The minimum variation for the case of sensitivity tests in each of the parameters is given by:

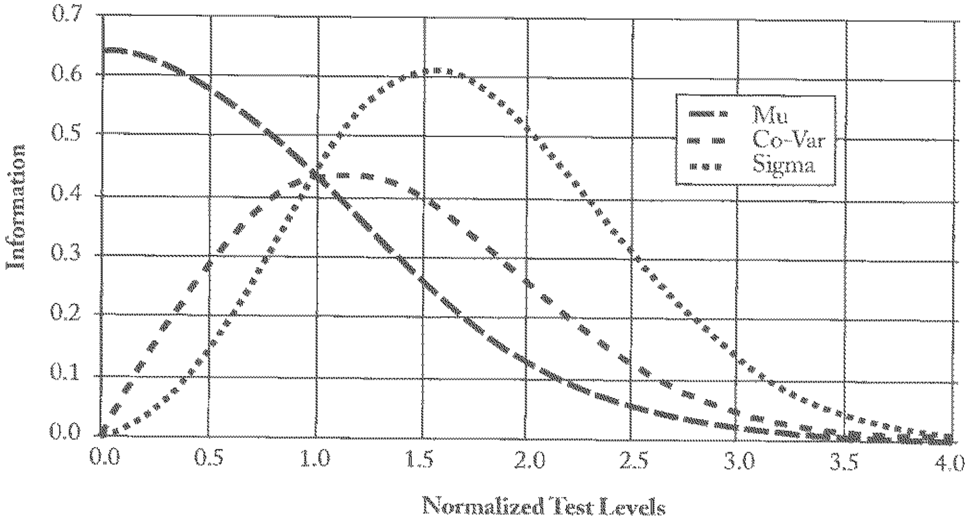

Figure 4-2. Normal sensitivity test information matrix functions.

$$\text{var}\, M \geqslant I_{11}/(I_{00}I_{11} - I_{01}^2) \qquad [4\text{-}2]$$

and

$$\text{var}\, S \geqslant I_{00}/(I_{00}I_{11} - I_{01}^2) \qquad [4\text{-}3]$$

where the I_{jk} is the information matrix[127], M is the estimate of the mean, and S is the estimate of the standard deviation. The information matrix is the sum of the information for each test point. The contribution of each test item to the information matrix is shown in Fig. 4-2. The I_{00} term is computed from the curve labeled Mu, the I_{11} term is computed from the curve labeled Sigma and the I_{01} term is computed from the curve labeled Co-Var. In most test designs the test points are chosen approximately symmetrically about the mean and the covariance part of the information matrix is close to zero. If the covariance is zero, then the variance of the estimate of the mean will be minimized by testing at the mean, and the variance of the estimate of the standard deviation will be minimized by testing at points ± 1.6 standard deviations from the mean. Thus, it is impossible to maximize information (minimize variation) about the mean and standard deviation simultaneously. (For output characteristics that can be measured exactly, the corresponding information contributions are exactly one for each test item. The information functions show how much less information is available for sensitivity types of tests.)

Test Methods

Over the years many different test methods have been developed to determine the initiation characteristics of a population of pyrotechnic devices as efficiently as possible. The guiding principle behind the design of these test methods has changed over the years, as our computational ability has improved.

Although test and analysis are independent functions, each discrete test method is historically associated with its own analysis technique. In most cases, any analysis technique can be used to analyze the results of a test conducted with any test method. There are some exceptions, such as the Bruceton analysis method, which is capable only of analysis of data taken using the Bruceton test method. The following sections will discuss the various test methods that have been developed. The later sections will discuss the analysis methods.

All of the tests, with the exception of the Probit test, make the assumption that the underlying distribution is known. It is usually assumed that the distribution of critical initiation stimuli follows a normal (Gaussian) distribution. In some cases, it is the logarithms of the stimuli that follow the normal distribution. The various test methods are described in the following sections. The test methods are described in the order that they were historically developed. This order is also the order of increasing efficiency.

Probit Test

The Probit[19] test was first described in 1935. The user tests a number of items at several fixed levels. Usually these levels are evenly spaced, but that is not a requirement. Six is a typical number of test levels, but any reasonable number can be used. Ten or more items are tested at each stress level. Unlike all of the other tests discussed here, this test is not sequential; all of the units can be tested simultaneously.

Because a large number of items are tested at each stress level, it is possible to convert the test results into a set of probabilities of initiation for each level. These probabilities are then converted to Probits. (A Probit is five added to the inverse of the cumulative normal function. Because the Probit method was developed long before electronic computers, the Probits were calculated with the help of a table.) The Probits are plotted versus the stress levels. Alternatively, the probabilities could be plotted on probability paper versus the stress levels. If the points lie along a straight line, then the assumption of normality is validated in the region of the test. The median (50% point) or any other probability level can be read directly from the line. The slope can be converted into an estimate of the standard deviation. If the points do not lie on a straight line, then there is often some simple transformation (such as the log of the stress) that will make the data appear linear.

The Probit method has the advantage of verifying the form of the distribution, at least in the center of the distribution. The Probit test also had the advantage that the analysis could be performed without difficult calculations.

The big disadvantage of the Probit test is that the test levels have to be chosen properly. The test levels should be chosen so that they span the 10% to 90% response region. Levels where 0% or 100% of the specimen respond cannot be used since those levels have a Probit value of minus or plus infinity. Because the purpose of the test itself is to estimate these levels, limited knowledge of the population will often lead to inappropriate choice of the test levels. The Probit test always requires a large sample size to achieve reasonable results.

Bruceton Test

The Bruceton test[54, 55] was developed in the 1940s to overcome some of the difficulties of the Probit test. Like all sequential tests, the test level for item *n* depends on the results of (some of) the previous items tested. The first sample is tested at a specified stress. If that sample responds (the pyrotechnic device fires) the next test sample is tested at a stimulus level that is reduced by a defined increment, or step, lower than the first. If the first sample had not responded, the next sample would have been tested with a stimulus increased by the same defined increment. The test continues in this process until at least forty items are tested.

The Bruceton test has the advantage that the tests are concentrated in the region of mixed response, i.e. in the 10% to 90% response region. Because the test levels are concentrated in this region, the Bruceton test is able to yield more statistical information than the Probit test from the same sample size.

The Bruceton test has an additional benefit in that it is simple to perform the analysis using pencil and paper. This test was also developed before the invention of electronic computers; the analysis had to be performed by hand. The mean and standard deviation, as well as their confidence levels, can be estimated by computing sums of squares. The efficiency of *calculation* was a major advantage of the Bruceton test, and the principal reason that it was quickly adopted. The specialized Bruceton analysis method is discussed in the analysis section.

The main disadvantage of the Bruceton test is that the efficiency of the test depends critically on a proper estimate of the step size. For maximum efficiency, the step size should be equal to the standard deviation of the population. If the step size is too small or too large by a factor of two, the efficiency drops off exponentially. Because the standard deviation of the population is typically unknown in advance of the test, the experimenter must guess at a proper step size. It is possible to perform a preliminary set of tests first to estimate the standard deviation to arrive at a suitable step size. However, as the analysis section shows, a very large sample size is required to arrive at a good estimate of the standard deviation. The Bruceton test concentrates the test points near the mean. This concentration provides a good estimate of the mean or 50% point, but is not efficient for estimating the standard deviation or the tails of the distribution that are typically required.

Robbins-Monro Test

The Robbins-Monro[197, 205] test was developed in the 1950s. It is similar to the Bruceton test in that it requires a starting guess and a step size. The difference is that the step size decreases as 1/N where N is the sample currently tested. This test method concentrates the test points at the mean. Thus, it is an efficient method of determining the mean level of the population, but it is very inefficient for determining the standard deviation and the tails of the distribution. The test can also be modified to converge on any desired probability level.

The Robbins-Monro test also has several advantages in terms of analysis. At each step, the next stimulus value is the estimate of the desired probability level.

The test is also distribution independent, at least in principle. However, since all of the test points are concentrated at one point, it is very inefficient for determining any population parameter except for the desired probability. Moreover, the ability to estimate reasonable confidence intervals for these parameters is severely limited.

Langlie Test

The Langlie[141] test method was developed in the 1960s to overcome the dependence of the Bruceton test on the choice of the step size. When the Langlie test was developed, computers were available to aid in the analysis of the test results, eliminating the restriction of pencil and paper *analysis* that guided the development of the previous tests. Instead, a test could be designed to use the specimens efficiently to arrive at the sample population parameters. However, the *test algorithm* still had to be easy to perform by hand because computers were not available in the laboratory.

To perform a Langlie test, the experimenter must specify lower and upper stress limits. The first test is conducted at a level midway between these limits. The following description of computing the next test is taken from the original paper by Langlie. "The general rule for obtaining the $(n+1)^{st}$ stress level, having completed n trials, is to work backward in the test sequence, starting at the n^{th} trial, until a previous trial (call it the p^{th} trial) is found such that there are as many successes as failures in the p^{th} through n^{th} trials. The $(n+1)^{st}$ stress level is then obtained by averaging the n^{th} stress level with the p^{th} stress level. If there exists no previous stress level satisfying the requirement stated above, then the $(n+1)^{st}$ stress level is obtained by averaging the n^{th} stress level with the lower or upper stress limits of the test interval according to whether the n^{th} result was a failure or a success."

The Langlie test is less susceptible to variations in efficiency caused by inaccurate test design. However, the efficiency of the test is somewhat dependent on the choice of lower and upper stress limits. Typically, extremely wide limits are specified to avoid situations where they do not contain the region of interest. The method is most efficient if the upper and lower limits are ± 4 standard deviations from the mean.

The original Langlie method is a very inefficient if there is a grossly improper choice of lower and upper limits. To overcome this deficiency, Langlie later proposed an adaptive test. The Adaptive Langlie test shifts the test limits up or down by one third of the range whenever the test levels converge on the upper or lower test limit. The Adaptive Langlie test is better able to overcome improper choice of test levels, but too small or too large a test range results in inefficient test level choice.

Both the Langlie and Adaptive Langlie tests concentrate the test levels very close to the mean. While this approach provides a reasonably efficient method of determining the mean level, it provides little knowledge of the standard deviation and the tails of the distribution. It also contributes to rather large confidence limits.

Neyer D-Optimal Test

The Neyer D-Optimal[175, 176] test was developed in the late 1980s. It was designed to extract the maximum amount of statistical information from the test sample. Unlike the other test methods, this method requires detailed computer calculations to determine the test levels. Thus, this method was not practical before computers became widely available in the laboratory. The Neyer D-Optimal test uses the results of all the previous tests to compute the next test level. The next test level is that level which maximizes the determinant of the information matrix. The test is designed to provide a complete characterization of the population.

There are three parts to this test. The first part is designed to "close in" on the region of interest, to within a few standard deviations of the mean, as quickly as possible. The second part of the test is designed to determine unique estimates of the parameters efficiently. The parameter estimates are unique once the responses and failures overlap. The third part continuously refines the estimates once unique estimates have been established.

This test requires the user to specify three parameters, i.e., lower and upper limits for the mean, and an estimate of the standard deviation. The first two parameters are used only for the first few tests (usually two tests) to obtain at least one response and one failure to respond. The estimate of the standard deviation is used only until overlap of the data occurs. Even if the guesses for the parameters are wrong, the algorithm will find good estimates of the parameters. The only penalty is that the first few items tested will be wasted as the algorithm finds the proper test space. Thus, the efficiency of the test is essentially independent of the parameters used in the test design.

Comparison of Test Methods

There is no unambiguous method of ranking the test methods. A good test method should yield estimates of the parameters of the population that are accurate and precise. All of the test methods yield accurate estimates of the mean, though the estimates of the standard deviation are biased low. Thus, the best way to rank the tests is by their precision. The purpose of most sensitivity tests is to determine an all-fire or a no-fire level. These levels are usually defined as that level at which at least 0.999 of the devices respond or fire (all-fire) or at which at least 0.999 of the devices fail to fire (no-fire). With the assumption of normality, the all-fire and no-fire levels can be converted into a simple function of the mean, μ, and the standard deviation, σ, of the population. The 0.999 all-fire level is $\mu+3.09\sigma$, and the 0.001 no-fire level is $\mu-3.09\sigma$. Thus, precise determination of the all-fire or no-fire level requires precise determination of the mean, and more importantly the standard deviation.

There are several ways to compare the ability of the various test methods to determine, with precision, estimates of the standard deviation. One method would be to determine the variation of the estimates of the standard deviation as a function of sample size and test method. This variation depends not only on the test method, but also on the selection of the parameters of the population before beginning the test.

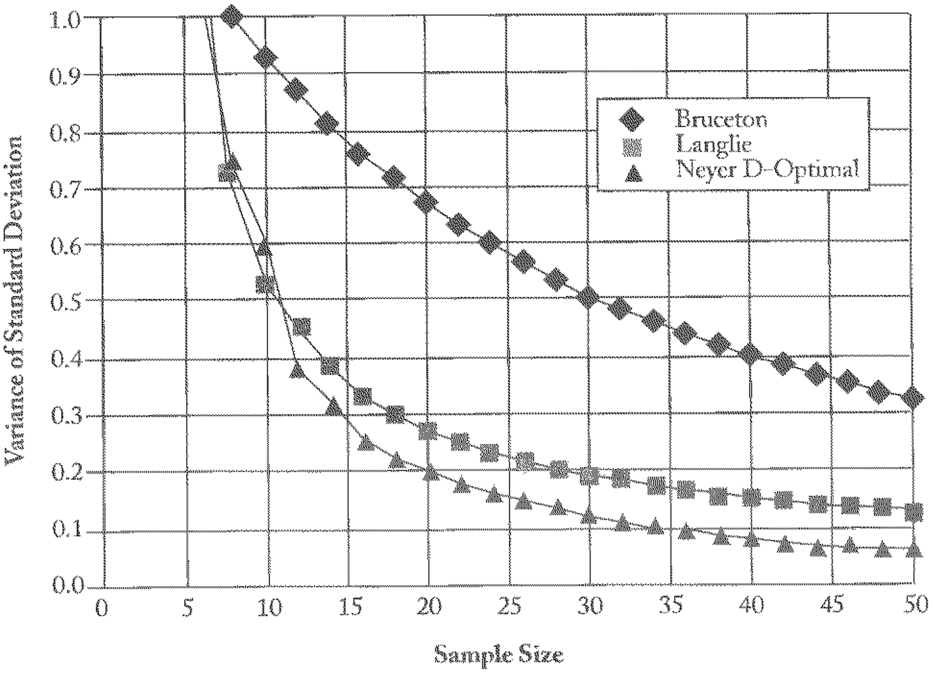

Figure 4-3. Comparison of the variation in estimates of the standard deviation.

The Probit method depends completely on how the test levels are chosen. The Robbins-Monro method is not used much in the field of pyrotechnics and will not be discussed further. The efficiency of the Bruceton test is strongly dependent on the choice of step size. The efficiency of the Langlie test is somewhat dependent on the spacing between the upper and lower test levels. The Neyer D-Optimal test is essentially independent of the choice of parameters.

Figure 4-3 shows the variation of the estimates of the standard deviation as a function of the sample size for the Bruceton, Langlie and Neyer D-Optimal test methods under the assumption that the standard deviation is well known before start of testing. If the items are well characterized from previous tests, the standard deviation may be known to within a factor of two. The figure assumes that the parameters of the test were optimized for the population.

It shows that variation of the estimate of the standard deviation has a strong dependence on the test method chosen. For example, a 20-shot Bruceton test yields a relative variance of 66%, while the Langlie test yields a variance of 28% and the Neyer D-Optimal yields a variance of 20%. The literature cited in this chapter provides more in-depth details of the analysis used to produce this graph. This graph is valid only when the correct test parameters are known. In particular, the variation could be much larger when using the Bruceton method.

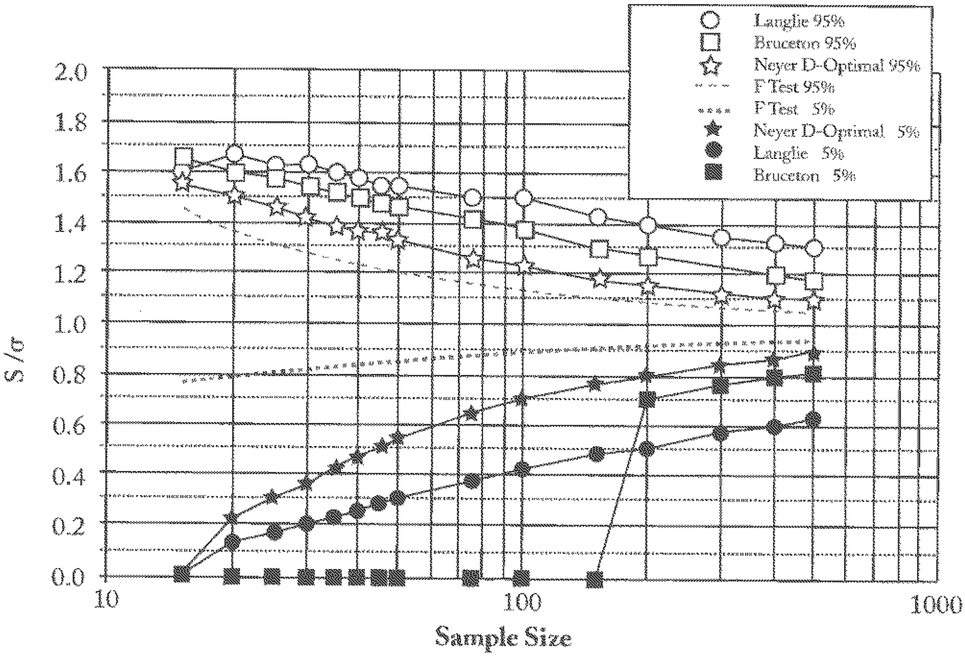

Figure 4-4. 5% and 95% estimates of the relative standard deviation.

In this case, it could be wrong by a factor of two if the estimate of the step size is wrong.

Another method of ranking the various test methods is to determine the extreme values of the estimates of a parameter. The greatest concern in conducting and analyzing sensitivity tests is the tendency of the method to produce estimates of the parameters that are far removed from the true parameters.

Fig. 4-4 shows 5% and 95% ratios of the estimate of the standard deviation divided by the true value as a function of the sample size for the three test methods. Also shown in the figure are the corresponding curves for the F Test, the significance of which is described in the text below.

The figure illustrates several important points. First, it is extremely difficult to establish the value of the standard deviation to the degree of precision desired with a limited sample size. For example, in a Neyer D-Optimal test with a sample size of 150, 5% of the estimates of the standard deviation will be more than 20% lower than the true value, and another 5% will be more than 20% higher than the true value. With the same sample size in the Langlie test, 5% would be 50% lower, and 5% would be 45% higher. For the Bruceton test the corresponding results are 100% lower, and 30% higher.

For the typical sample size used in threshold tests, *e.g.*, 20 - 50, it is impossible to estimate the standard deviation, and thus the all-fire and no-fire levels, with great certainty. Thus, in addition to estimating the parameters of the population, it is also imperative that the appropriate analysis be performed to estimate the confidence level of the estimate of the parameters. Confidence estimation is discussed in the next section.

The F Test curves shown in Fig. 4-4 indicate how much less information is available for sensitivity tests compared to standard statistical tests. The F Test is used in standard statistical testing to calculate the fraction of estimates of the standard deviation that are higher or lower than a given value. If it were possible to measure the exact threshold of individual items, then the estimates of the standard deviation would be governed by the F Test. Inspection of the curves shows that a sensitivity test requires a sample size many times greater than the sample size of a classical statistical test to achieve the same range of values for the standard deviation.

Finally, the figures illustrate that the ability to determine reasonable estimates of the parameters is extremely dependent on the test method chosen to conduct the test. Both Fig. 4-3 and Fig. 4-4 illustrate the importance of choosing an efficient test method when conducting sensitivity tests.

The most efficient test method should ALWAYS be chosen. Using any other test method will require a larger sample size to achieve the same precision as the most efficient test. Thus, of the methods listed, only the Neyer D-Optimal method should be used to conduct sensitivity tests.

Analysis Methods

More methods of analyzing the results of sensitivity tests have been proposed than have test methods. The method chosen to analyze the data of the test is at least as important as the test method. While many analysis methods can be used to analyze the results of any test method, other analysis methods are designed to analyze only one test design. All of the analysis methods provide relatively unbiased estimates of the mean, M; the estimate of the standard deviation, S, is generally biased too low. However, the ability of the various methods to compute reliable confidence levels varies greatly.

Simulation discussed in some of the referenced papers shows that the variance of both M and S scales approximately with σ^2. Because σ^2 is not independently known, all of the analysis techniques (except the Likelihood Ratio test) base their estimates on the maximum likelihood estimate of σ. If the successes and failures do not overlap, $S = 0$ and these methods fail to produce estimates for confidence regions for either M or S.

Variation Function Analysis

The variance function method assumes that the variances of M and S can be estimated by simple functions of the sample size and the standard deviation. These functions are generally dependent on the initial conditions, sample size, and the test design, i.e., Bruceton, Langlie, or Neyer D-Optimal. Some experimenters use the students-t distribution test method to compute confidence intervals for the mean, and Chi Squared or F tests to compute confidence intervals for the standard deviation. However, these generalized statistical methods should not be used to estimate the reliability of the sensitivity test used. That is, the assumptions that are used to construct general statistical tests are violated in the case of sensitivity tests. Fig. 4-4 shows the curves for the F test as well as curves for the various sensitivity tests. The figure clearly shows that the F test cannot be used to analyze sensitivity tests. Because there is no generally accepted formula that works for all cases, this method is not in widespread use.

Simulation Analysis

The simulation method uses the estimated parameters from test results to perform a number of simulation runs. These runs determine the variance of the parameters given parameters similar to those estimated from the experimental data. This method can provide reliable estimates of the variances as long as the simulation is carried out with parameterization relevant to the population. If simulation is used to estimate the variation of the parameters, the parameters for the simulation must span a wide area around the estimates of the test data. The number of simulation runs must be sufficient (well over 1000) to ensure that the results are statistically valid. Because of the difficulty of performing such simulations, this method is not in general use.

Bruceton Analysis

The Bruceton Analysis method was co-developed with the Bruceton test. It was designed so that simple paper and pencil calculations could be used to determine the mean and the standard deviation, as well as estimates of their variance. It uses the same approach as the asymptotic method of the next section, but with some simplifications that are possible for the highly structured Bruceton test. The Bruceton analysis method can only be used to analyze the results of tests conducted strictly according to the Bruceton test method.

Today, more advanced analysis methods are available to analyze this data. The traditional Bruceton analysis method can still be used, but only when the number of test levels is between 4 and 6, and the sample size is large. In all cases it is preferable to use more advanced analysis methods, such as the ones described in following sections. When the Bruceton analysis is valid, it gives essentially the same results as the asymptotic method.

Asymptotic Analysis

Asymptotic Analysis is the method used in many computer programs known as ASENT[10]. This software is in use at many test facilities. Similar software with different names has also been developed in other laboratories. Although this analysis method is often associated with the Langlie test method, it can analyze the results of tests conducted according to any test method. The analysis method computes the maximum likelihood estimates of the parameters. It computes estimates of the variance of the parameters by computing the curvature of the likelihood function. This analysis method gives the correct results asymptotically. It will not analyze the results of a test where the successes and failures do not overlap. It gives reliable results if the sample size is greater than 200.

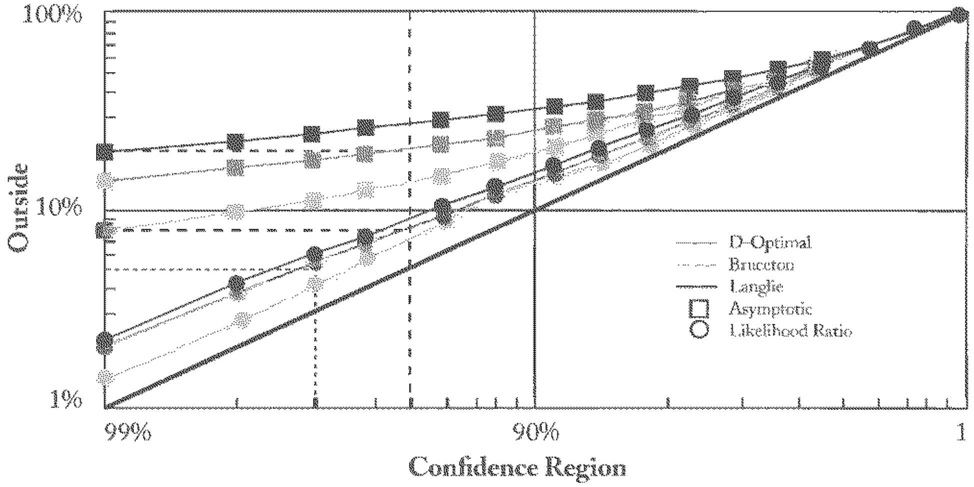

Figure 4-5. Comparison of confidence likelihood ratio versus asymptotic analysis.

Likelihood Ratio

The Likelihood Ratio test[177] is in use at many laboratories around the world. Because it was developed at the same time as the Neyer D-Optimal method, it is often associated with that test. However, it is a general analysis method and can analyze the results of tests conducted using any test method. The technique computes the maximum likelihood estimates of the parameters the same way as the Asymptotic Analysis method. It computes estimates of the variance of the parameters by using the Likelihood Ratio test. This analysis method gives the correct results asymptotically. Because it does not rely on an estimate for the standard deviation, it will analyze the results of any test, even if the successes and failures do not overlap. It gives reliable results if the sample size is greater than 20.

Comparison of Analysis Methods

The two most widely used general analysis methods can be compared in a number of ways. (The Bruceton analysis results, when valid, are essentially identical to the asymptotic results and are not given separately.) The most meaningful way to compare the methods is to determine what fraction of the time the true parameters are outside of the specified confidence region. A properly computed 95% confidence region, for example, should contain the true parameters approximately 95% of the time.

Fig. 4-5 shows the fraction of parameters outside a given confidence region for both the Asymptotic Analysis used by ASENT and the Likelihood Ratio Analysis. This figure was generated for a sample size of 30 for the Bruceton, Langlie, and Neyer D-Optimal tests. The solid line in the figure is what a perfect analysis method would produce. For each analysis method the upper line is the Langlie method, the next lower is the Neyer D-Optimal method and the next is the Bruceton.

In Fig. 4-5, all curves are above the solid line, indicating that both of the analysis methods produce false confidence. For example, for a nominal 95% confidence region, the Likelihood Ratio test has the parameters outside of the confidence region approximately 8% of the time. While this is more than the 5% expected for a true 95% confidence region it is close to the requested confidence. Note that it would be prudent for the user of this information to specify a slightly more restrictive confidence (such as 97%) to achieve the required 95% confidence region. Fig. 4-5 is valid for sample sizes of 30 only. A different sample size would produce a different graph, but with similar trends.

The asymptotic 95% confidence region however, has the parameters outside of the confidence region approximately 20% of the time, with the percentage a strong function of the test method. To achieve a true 95% confidence region using this analysis method would require the computation of a confidence region much greater than 99%.

Pyrotechnic devices that are considered reliable or safe when analyzed according to one analysis method might be considered unreliable or unsafe when analyzed according to a more exact analysis method such as the Likelihood Ratio test. Thus, it is crucial when reporting analysis to specify the analysis method.

The most realistic analysis method should always be used to analyze the results of sensitivity tests. Fig. 4-5 shows that the Likelihood Ratio method is capable of constructing reasonable confidence intervals, while the Asymptotic Analysis method produces false confidence. Thus, the Likelihood Ratio Analysis method should always be used instead of the Asymptotic Analysis method.

Chapter 5

Mechanisms and Rates of Pyrotechnic Reactions

An inquiry into the mechanisms of pyrotechnic reactions involves asking how they proceed. This is by no means a trivial question, because (with few exceptions) the starting materials are solid, and most are, by themselves, stable. Yet, the reactions are rapid and highly energetic. Over the years, many attempts at providing a general theoretical foundation have been made. These have been generally unsatisfactory in predicting the performance and functioning of pyrotechnic devices. Curiously, some of the most useful work was not done by pyrochemists, but by metallurgists and ceramicists, on related solid-state reactions with low (or even negative) energy output which are slow and amenable to study.[87] Many reactions that have been studied have in common the fact that they can be stopped by cooling and the mechanism can be studied by examination of the phase distribution in the product. Pyrotechnic reactions have been neglected because they lack reversibility and the reaction products are generally a matter of no interest. Pyrotechnic reactions must be studied in short time frames, relying on the rates of energy release, temperatures, and spectral data.

Pyrotechnic reactions rarely proceed to completion as solid-solid reactions, although some instances are known. However, in many cases, the "pre-ignition step" is a solid-solid reaction. In most of the latter reactions, the heat produced will be sufficient to melt one or more of the components locally, with a resultant acceleration of the rate. These solid-liquid reactions will be examined later in further detail. The reaction may cause decomposition of a reactant with the formation of a gas, or the reaction may take place in the gaseous phase. These reactions are harnessed in propellants, but are also found in flares, photoflashes, and tracers.

Solid-Solid Ignitions

Pre-ignition Step

Differential thermal analysis for most pyrotechnic mixtures shows a slow and gradual exotherm, sometimes commencing at temperatures hundreds of degrees below the exotherm commonly associated with the ignition temperature. This energy output is observed to be independent of pressure, showing that it is not brought about by reaction with atmospheric gases, and is not associated with a reversible chemical reaction. This exotherm is not observed when the components are heated separately, and is generally not therefore considered dependent on the surface conditions or methods of preparation of the materials. This phenomenon is especially interesting in metal/metal oxide systems such as thermites, and may be caused by contamination with oxides or other trace impurities which act to increase the mobility of the reactive species, even at low temperatures. For instance, the pre-ignition step of a Ti/CuO mixture commences at about 500° C, about 250° C below the ignition temperature. Even at 750° C, the temperature is too low to account for the presence of molten titanium or copper to act as solvent (see below), although once the reaction commences even on a microscopic scale, the vapor pressure of copper is sufficient to cause molten or vaporized copper to act as flame carrier. The pre-ignition phenomenon provides an insight into the mechanism which makes possible the chemical reaction of solids when classic rate studies (as by the Arrhenius model) would predict negligible reaction. This writer has found that boron and silicon[98] are particularly effective in lowering the initiation temperature of mixtures with metallic elements, probably because of the high concentration of serendipitous impurities. Ultra-pure boron and silicon are not as reactive as are the commercial pyrotechnics grades.

The reasons for this observation might be examined by looking at lattice defects which exist when either vacancies or interstitial ions are present in the crystalline structure. It is not really necessary that the concentration of defects be high, because a distorted lattice may act as if the crystal had non-stoichiometric properties. In boron and silicon, the likelihood of such defects is high because the method of preparation by oxide reduction or vapor phase deposition generates many defects which cannot be removed except by special techniques of refinement.

Another fuel the reactivity of which is dependent upon physical structure is amorphous carbon – charcoal, lampblack, or one of the gas or vegetable blacks. A common technique in civilian fireworks is to add a small percentage of one of these ingredients to enhance ignitability and burning speed. Five per cent or less is typically efficacious in potassium perchlorate/resin fuel color stars; the upper limit is established by the onset of deterioration in the purity of the color.

Defect structures can be induced during the preparation of oxides. For instance, the reactivity of iron oxide is higher when it is made by pyrolysis of ferric sulfate than when it is made by pyrolysis of ferric oxalate.[161] Still more reactive is magnetic iron oxide, which when ball milled with aluminum in a planetary mill can be made to ignite dry, a phenomenon to which the writer can attest from personal experience. A method of increasing the reactivity of some specific mixtures is by co-precipitation[168], as further discussed in Chapter 18.

Examples of Solid-Solid Reactions

The study of pyrotechnic reactions is closely related to the study of ignition (see Chapter 9). Ignition occurs when the local rate of an exothermic reaction produces heat faster than it can be lost to the immediate environment. Self-sustaining solid-solid reactions, such as the formation of tantalum carbide or tantalum boride from the elements, are only possible if the particles are very fine (<5 μm), because the rate of these reactions is diffusion-limited. Larger particles cause these reactions to be incomplete[81] because as the initial temperature spike from the ignition dissipates, the reaction quenches. If both reactants and products are solid at the reaction temperature, the mechanism resembles sintering. Diffusion coefficients for sintering range from 10^{-7} to 10^{-15} cm^2/s.[193] Solid-solid reactions are often "solid" in name only. Oxide contaminants provide a liquid or gaseous interface. With boron, the oxide is liquid at comparatively low temperatures (450° C), as are silicates (for lead silicate, mp. = 766° C). True solid-solid reactions are rarely suitable for pyrotechnics because they are neither energetic nor sufficiently rapid.

Solid-Liquid Reactions

Many pyrotechnic reactions take place upon the melting of a reactant or product at the ignition temperature. Diffusion coefficients for a liquid are typically five orders of magnitude higher than for a solid (*i.e.*, 10^{-2} - 10^{-6} cm^2/s). Also, reactants are much more soluble in the liquid than in the solid so that reactions, if energetic, are rapid and self-propagating. Such reactions may be intermetallic[80, 100], or, as described above, thermite reactions. It is characteristic that the rates of solid-liquid reactions are not affected by pressure. Note that it makes no difference to the reaction whether products are solid at room temperature or not, but only what the state is at the reaction temperature. For instance, when the boron/barium chromate and tungsten delay mixtures are compared (see Chapter 18), tungsten delays are seen to have a significant concentration of volatile tungstic oxide and of volatile tungsten and chromium oxychlorides in the flame front.[263] The boron/barium chromate system is a liquid/solid system (because of the presence of low-melting boric oxides), while tungsten delays are gas/solid systems.

Ignition of a solid-liquid reaction may involve mass transport in the solid phase, induced by a thermal spike from the igniter. Ignition will cause the temperature at the flame front to rise to approach the adiabatic reaction temperature (see Chapter 7) resulting in the melting of a constituent, hence the formation of a liquid phase. The rate-determining step is the wetting of the solid particles by the liquid, making possible rapid and efficient mass transport. Capillary action assures uniformity of liquid distribution. Reactants which have only limited solubility in the solid at ambient temperatures may yet dissolve in the liquid to a significant extent.

The rate expression for a condensed phase reaction (*i.e.*, solid-solid or solid-liquid) is of the Arrhenius type:

$$\rho \frac{\partial f}{\partial t} = \rho \frac{A}{n} (1-f)^{n-1} \qquad [5\text{-}1]$$

Where T is the reaction temperature
t is time
ρ is density
A is the preëxponential coefficient
n is the rate law exponent $\left(\frac{-E_a}{RT}\right)$
R is the gas content
f is the fraction unreacted
E_a is the activation energy

The magnitude of the activation energy provides insight into the mechanism. For solid diffusion-controlled reactions, the activation energy is on the order of 40-80 kcal/mol, while for solid-liquid reactions, the energy is lower, 10-40 kcal/mol.

If the propagation rate, v expressed in cm/s, is assumed to be dominated by heat transport (as is usually the case) and not by mass transport, one may assume that the fraction reacted, $(1\text{-}f)$, immediately ahead of the reaction front, is zero, and that the rate law exponent will be zero ($n=0$). Otherwise the exponent is $n=1$. This means that the reaction rate, $\partial f/\partial t$ is very high, and that the reaction will go on to completion in the reaction zone, within milliseconds. The effect of the various parameters on the propagation velocity was modeled[94] and it was found that the rate was, as a first approximation, independent of activation energy, density, ambient temperature, tube diameter and design, but strongly affected by thermal conductivity. The analytical finding was confirmed experimentally for the Pb_3O_4/Si-Al and B/$BaCrO_4$ systems by McLain[161]. Calculation of the propagation rate is complex because of the partial differential equation which describes the temperature distribution in the reaction mass:

$$C\rho\,\frac{\partial T}{\partial t} = \lambda\,\frac{\partial^2 T}{\partial x^2} + Q\rho\,\frac{\partial f}{\partial T} \qquad [5\text{-}2]$$

where: C is the heat capacity, cal/g °C
λ is the thermal conductivity, cal/cm s °C
Q is the heat of reaction, cal/g
ρ is the density, g/cm^3

Exact solutions of Equation 5-2 are not possible because both temperature and time vary with depth into the mass. The current practice is to provide computer solutions of the temperature profile as a function of depth[98] and to use the change of depth with time as a measure of the propagation rate. Propagation rate expressions have been reported[166] which have the appearance of a Maillard and Le Chatelier equation:

$$v = \frac{\lambda Q}{a C^2 \rho (T_a - T_o)} \qquad [5\text{-}3]$$

where: v is the propagation rate
a is the reaction zone width, [see Equation 5-4], cm
T_a is the adiabatic reaction temperature, K
T_o is the ambient temperature, K

This equation reduces to Equation 5-4 if $T_a - T_o$ is replaced by Q/C. Equation 5-4 also shows that the propagation of condensed phase reactions is not a function of compaction, *i.e.*, $v\rho \neq \Phi(\rho)$.

These discussions must not be interpreted to mean that the performance of any pyrotechnic device can be predicted *a priori* from the materials' properties. On the contrary, the performance must be tested for each mixture, for each method of fabrication, and for each environmental condition – the theoretical analysis is at best an aid for data analysis. For instance, by plotting the propagation velocity against the reciprocal of the reaction temperature, T_a, propagation rates may be extrapolated. Likewise, the particle size effect, as well as the effects of thermal conductance, density, and heat output can be studied.

Solid-liquid reactions, when proceeding in a pressed grain, take place in layers. The reacted product has a distinctly layered appearance, with the thickness, s, of the layer being equal approximately to the reaction zone width:

$$s \approx \frac{\alpha}{v} \qquad [5\text{-}4]$$

where α is the thermal diffusivity, $\lambda/C\rho$, in cm^2/s.

This equation is useful for estimating thermal difficulties from the propagation rate and the measured thickness of the layers. Layerwise reactions have been studied extensively by Merzhanov and coworkers[82] and by this writer[101] who find that the lower the reaction rate, g/cm^3s, (and hence, the lower the propagation rate) the thicker the layers become until eventually the reaction quenches. Another way to view this finding is that at the limit the reaction becomes a solid-solid reaction, just before quenching.

Another interesting reaction system is intermetallic. Examples include the synthesis of borides,[147] carbides, and aluminides of the transition metals by binary reactions. Originally, the main application in pyrotechnics was in Pyrofuze,[100] a product consisting of palladium-clad aluminum wires or sheets. The mechanism is a highly exothermic, diffusion-limited reaction between the elements forming a compound via a layerwise reaction. Another pyrotechnic application of intermetallic reactions is the addition of nickel powder to thermite mixtures[110] which can then be made to ignite around the melting point of aluminum (650° C) through the exothermic formation of a small amount of nickel aluminide.

Recently, titanium/boron mixtures have been of increasing importance as ignition compositions and are representative of the technology of self-propagating, high-temperature synthesis (SHS). The latter is a new development in pyrochemistry which seeks to fabricate materials such as grinding compounds and objects by synthesis of the refractory compound from the elements.

Solid-Gas Reactions

Whereas condensed phase reactions are usually mass transport (diffusion) limited, solid-gas reactions are usually kinetically limited. For instance, in studying the reaction of a metal with an inorganic oxidizer (such as a nitrate or chlorate) the kinetics of the decomposition of the oxidizer must be considered and Equation 5-1 must be modified accordingly. Surprisingly, decomposition rate constants for inorganic salts are not commonly published, in part because impurities and mixture components act as catalysts, and reaction rate data must be determined by differential thermal analysis (DTA) or thermogravimetric analysis (TGA) as described in Chapter 8. In practice, reaction rates of metal-oxidizer mixtures are always determined empirically. Certain oxidizers, such as chlorates and perchlorates, react with fuels to form volatile oxychlorides, chlorides, and oxides so that any rigorous kinetics study would be highly doubtful, even if stability data were available.

The largest group of solid-gas systems contain hydrogen and carbonaceous material and these serve as gas generators. The reaction takes place in the gas phase in a boundary layer above the substratum. The analysis of this type of reaction is associated with the work of Kuo and Summerfield[136]; a detailed presentation of this reaction model is beyond the scope of this book.

The propagation rate of a solid-gas reaction is approximated by the expression:

$$r = \mathrm{a}\,P_c^{\,\mathrm{n}} \qquad [5\text{-}5]$$

where: r is the burning rate, cm/s
P_c is the chamber pressure, atm
a is a constant in the range 0.05-0.002
n is a constant in the range 0.4-0.85

There are pyrotechnic reactions whose rates relate in a complex manner to a combination of the above mechanisms. For instance, motion picture studies of the burning of a magnesium/sodium nitrate flare have shown that the endothermically decomposing nitrate grain (in which the spherical magnesium particles are imbedded) generates gaseous nitric oxide and sodium oxide, which expel the magnesium particles. The surface oxidizes, generating heat which vaporizes the magnesium in the interior, and upon being vented, it reacts with the oxidizing atmosphere in the boundary layer, generating radiant heat which further decomposes the nitrate. Flares and tracers are not burned under pressure, but the pressure effect in such reactions would no doubt be a large one. One might assume that the pressure effect will be similar to that found for pressed black powder grains (*e.g.*, in model rockets) which have two burning rates, depending on pressure[201]:

$$r_1 = 0.871\ P_c^{\,0.461} \text{ where } 1.7 < P_c < 5.1 \text{ atm}$$

$$r_2 = 1.48\ P_c^{\,0.133} \text{ where } 5.1 < P_c < 27.2 \text{ atm}$$

Another interesting example of gas-solid reactions is that of the magnesium/Teflon system, which is of importance both as an igniter and as an infra-red (decoy) illuminant. The volatility of the reaction products in the flame front enhances ignitability and speeds up reactions by providing a mass and heat transfer medium. This is also true of reactions considered "gasless" because they have reaction fronts which are anything but gasless. For instance, in the aluminum/copper oxide first-fire, the highly exothermic reaction results in the formation of gaseous copper, the condensation of which in front of the reaction zone, provides an effective means of heat transfer. Flame transport by hot particles is highly desired and is the reason for selecting black powder or zirconium-containing mixtures for ignition. Yet none of the existing theories of ignition provide for this mechanism. Until this effect is quantified, ignition theories will be incomplete.

Halides are as a rule more volatile than oxides so that the addition of a halide donor accelerates the reaction, even if the reaction temperature is lowered by the endothermicity of the halide decomposition. There is another important reason for the halide addition which is discussed in more detail as part of the flame coloration problem. Halides volatilize some refractory oxides and produce a transparent flame which in turn will exhibit a stronger color.

Still another method for enhancing ignitability and accelerating reactions consists of selecting oxidizers which have a low melting point. When one component dissolves another without reaction, the melting point of the solution is lowered until an eutectic composition is reached. A study of eutectic mixtures of oxidizers discloses low melting combinations which can be prepared and used safely. The resulting eutectic mixtures can be blended with the fuel and may result in compositions which initiate at lower temperatures and which react more rapidly than do mixtures with single oxidizers. One of Bowden's patents[23] illustrates this point: the eutectic mixture of potassium, sodium and lithium nitrates is claimed to produce a black powder which burns faster than the standard material. Table 5-1 is a list of various nitrate mixtures.

Table 5-1. Melting Points of Nitrates and their Eutectics

Percent by mass of Nitrates*	M.P., °C
100 Li	255.0
100 Na	308.0
55 Li, 45 Na	198.0
100 K	333.0
34 Li, 66 K	129.0
45 Na, 55 K	225.7
30 Li, 16 Na, 54 K	119.0
100 NH_4	170.0
78.2 NH_4, 21.8 Na	121.1
66.5 NH_4, 21 Na, 12.5 K	118.5
100 Urea	133.0
18.8 Li, 81.2 Urea	71.0
50 Li, 50 Urea	98.5
100 Ag	212.0
25 Li, 75 Ag	171.5
20 Li, 61 NH_4, 19 Ag	52.0
8 Na, 55.5 NH_4, 36.5 Ag	95.0
12 Na, 67.5 NH_4, 20.5 Ag	94.0
100 Tl (monovalent)	206.0
12.5 Li, 87.5 Tl	136.5
100 Rb	310.0
18 Li, 82 Rb	154.0
46.5 Li, 53.5 Rb	179.5
32 Na, 68 Rb	178.5
100 Cs	414.0
32 Li, 68 Cs	174.0
100 Ca	561.0
70 Li, 30 Ca	235.2
30.5 Li, 40 Na, 29.5 Ca	170.3
23 Li, 62 K, 15 Ca	117.4
11.8 Na, 39.4K, 48.8 Ca	133.0

* The chemical symbols stand for the metallic nitrate, whereas 'urea' stands for the compound itself. These data were taken from the Technical Data Sheet TD-105 (Foote Mineral Company) and Mellor, where in Supplement II, Part II, p. 1250*ff*, are listed also the eutectics with alkali dichromates.

Chapter 6

Color Creation

No treatment of pyrotechnics can attempt completion without an examination of the phenomena of color generation. The matter is worth consideration because the requirements for the practical attainment of æsthetic and useful results are by no means simple. It is here that application of physical theory to the needs of pyrotechnics has done most to reduce the need for lengthy formularies based upon exhaustive trial and error. Much is owed to the current generation of practitioners, particularly Dr. Takeo Shimizu[215, 216] in Japan and R. G. Cardwell *et al.*[194] in the U.S.A. for making available more information about the current state of the subject.

There is an abundance of useful data on color visibility in the *Military Pyrotechnics* series[169] which also extensively treats the physical principles of color perception with military requirements in mind. The current emphasis on pyrotechnic effects in the infrared range for signalling and decoy purposes has shifted the focus from the study of subjective physiological responses to instrumental analysis and detection. Most people associate the term "pyrotechnics" with fireworks. Indeed, the most memorable aspect of fireworks is the diversity of visual effects in terms of brightness, color, and spark effects. While certain types of fireworks are quite common, nothing in pyrotechnics is as difficult as the creation of reproducible visual effects.

The visible colors can be described by the characteristic frequency ranges (Table 6-1).

Table 6-1. Wavelength Ranges of Spectral Colors[174]

Color	Wavelength, nm
Infrared	>700
Red	700–610
Yellow	610–570
Green	570–500
Blue	500–450
Violet	450–400

Light emitted within a particular wavelength range can reasonably be described as monochromatic; yet when colored light is generated pyrotechnically, it is not monochromatic, because it also contains spectral components outside the desired spectral range. Therefore, most pyrotechnic colors are not "spectral colors" characterized by a narrow cluster of wavelengths, but are perceived through physiological responses. The reason pyrotechnic flames behave in this manner is that the photon emission is characteristic of the decay of the electron excitation. Atoms, when excited by high temperatures, produce several strong emission lines, both within and outside the visible range. Only a few elements have principal emission lines lying within a narrow visible range. Multiplicity of emission lines in the visible range causes the color to become impure and "washed out." The other reason for the complexity of pyrotechnic colors is that the flames contain a high density of ions and free electrons. The decay of their excitation does not exhibit monochromatic emission. Upon cooling, electrons and ions recombine and their excess energy is carried off as photons. Because free electrons and ions start with a continuum distribution of energies, the emitted photons will be seen as a continuous spectrum and therefore perceived as white light. The more intense this continuous spectrum is, the weaker the perceived color. Therefore, *atomic* line spectra are not the best source of color, except for the yellow of sodium and perhaps the infrared colors of other alkali metals, the flames of which owe their brightness to "line broadening" (see Chapter 17). Many ionized species exist in the gaseous phase as bi- and tri-atomic molecules which give off molecular band spectra that arise from the ability of the molecule to absorb vibrational and rotational energy. Because molecules have fixed masses, sizes, and interatomic spacings, their rotational and vibrational energies are also quantized and so can take up and emit energies in discrete wavelengths. To the extent that these band spectra are in the visible range, they are of interest in pyrotechnics. Molecular band spectra are stronger than atomic line spectra because they exist over a wider spectral range and thus give the illusion of a "purer" color.

Additives are necessary in pyrotechnics as "color intensifiers" except in the case of sodium yellows. Molecular spectra are useful because they provide insight into the structure of the molecule and its energy of formation, among other thermodynamic data. The molecular species that give the best colors are the halides of the alkaline earths and copper. The halides of other elements do not emit in the visible region, but may emit in the infrared. The energy bands, listed in Table 6-2, are by no means of equal intensity, but many of them are found in tight clusters and so appear as a stronger light rather than a pure color.

Triangular graphs for illustration of the relative quantities of fuel, oxidizer and additive are a great aid for demonstrating that there is really no perfect composition for the attainment of a pyrotechnic color, but that most mixtures are useful through a range of ratios. Quite a number of these have been published by Shimizu.[194, 215]

Table 6-2. Spectra of Simple Molecules of Interest in Pyrotechnics[112]

Molecule	Wavelength, nm
BaCl	910.0
BaCl	842.0
BaF	712.2
BaF	711.0
SrBr	680.2
SrCl	674.7
SrBr	666.5
SrCl	661.5
CaBr	628.0
CaBr	625.5
CaCl	621.3
CaCl	618.6
CaF	606.6
CaF	603.8
CaCl	593.5
CuF	569.6
BaI	561.4
SbO	543.3
BaI	538.5
BaBr	536.1
CaF	530.9
BaCl	524.6
CuCl	526.4
BaBr	521.0
BaCl	514.0
BaOH	512.0
CuI	507.4
CuF	506.7
CuCl	488.3
CuBr	488.1
BaOH	487.0
SbO	486.8
CuI	459.8
BiCl	459.6
PbCl	458.1
PbF	444.2
BiF	436.8
BiF	434.2
CuBr	434.2
CaI	429.0

Several systems have been devised for measuring color values. In 1931, the Commission Internationale de l'Éclairage (C.I.E.), also known as the International Commission on Illumination (I.C.I.) recommended the use of the tridimensional stimulus system, resulting in the Standard Colorimetric Coördinate System, or the X, Y, Z Color Triangle (see Fig. 6-1 and PLATE I). Another well-known approach is the Munsell color system, which gives the Munsell hue, value, and chroma of an unknown color by interpolation with Munsell color charts. Finally, color may be estimated by reaction temperature or wavelength (see Table 6-1). The Munsell color system is more subjective, whereas the C.I.E. system lends itself to being quantified. One can take a spectrum of the source with a spectrometer, and, after manipulation of the data, compute the X, Y, Z chromaticity coördinates, dominant wavelength, and purity. The results can be plotted automatically on the chromaticity diagram. Software programs exist to average the output of spectrometers, interferometers, or other devices used to obtain the spectrum of a source, thereby allowing for easy amplitude and wavelength calibration from standard sources. The C.I.E. coördinates are obtained by comparing the acquired spectra with curves stored in memory.

The tridimensional color stimulus values have been determined as a result of color comparison in tests conducted on many observers and compiled in order to estimate the sensitivity of the "Standard Observer." The XYZ color triangle is intended to reflect a quantitative measure of the three I.C.I. primary colors (red, green, and blue) to match the amount of energy observed from an equivalent monochromatic source. Because the intensities of the three primaries add up to unity, only the values of x and y need be plotted on the chromaticity diagram where

$$x = X/(X+Y+Z)$$

$$y = Y/(X+Y+Z)$$

and X = intensity of blue,
Y = intensity of red,
Z = intensity of green.

The center of the triangle (C) is the point of "white light" and corresponds to average daylight. While in practice it is difficult to assign tri-stimulus values without elaborate instrumentation, the scheme holds a certain attraction for pyrotechnists because it allows one to visualize the effect of blending certain colors. For instance, the line drawn between 380 nm and 700 nm forms the base of the triangle, which is called the "purple line," along which no perceptible color exists. Therefore, if one desires a purple color, care must be exercised in blending the colors at the extremity of the line lest the "C" point be approached and the color become "washed out." Much effort and skill are required to produce a purple flame as was documented by T. Shimizu[220] and R. M. Winokur.[257] In fact, the colors are described as "violet, lilac, reddish purple, carmine purple, crimson and mauve".

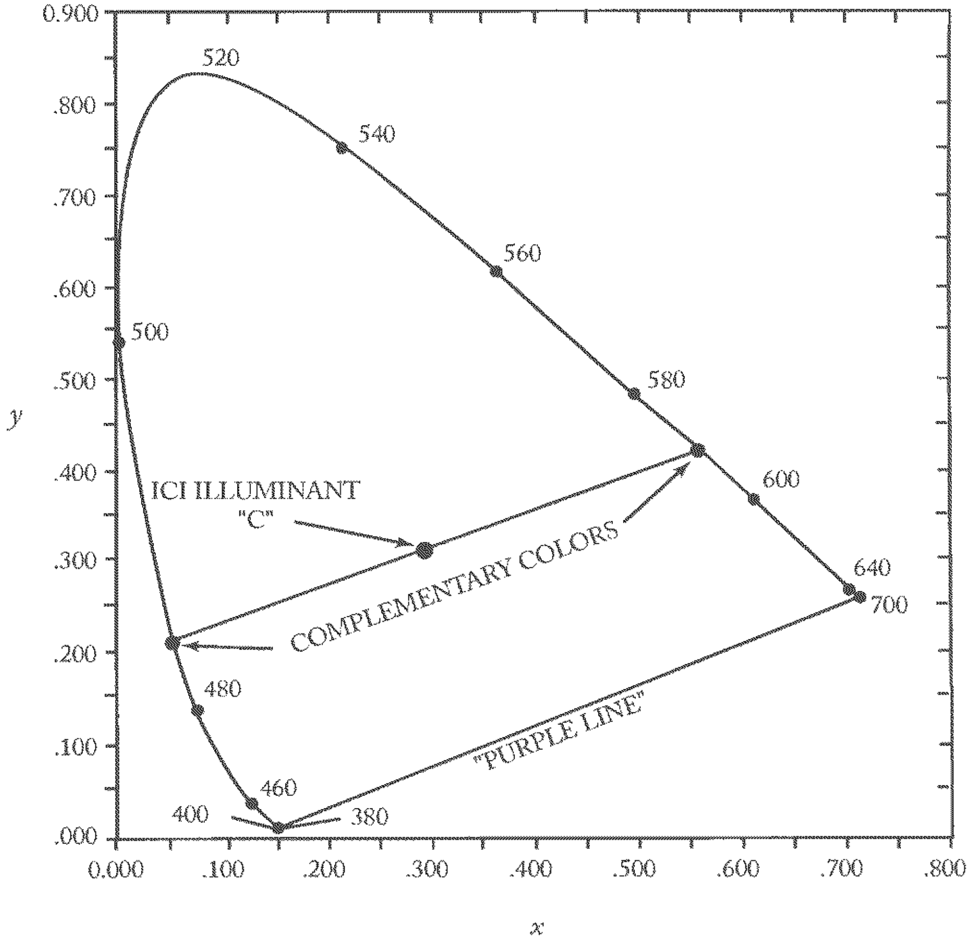

Figure 6–1. C.I.E. chromaticity diagram [*See also* PLATE I].

Chapter 7
Thermochemical Calculations

Before questions can be answered regarding a pyrotechnic reaction's rate, temperature, and reaction mechanism, one must determine energy output. Thermodynamics is one of the few aspects of pyrotechnics that permits accurate prediction of performance from published data. Toward this end one should have access to a good compilation of thermodynamic data. Convenient sources are the Chemical Rubber Company's *Handbook of Chemistry and Physics*[149a], and Lange's *Handbook of Chemistry*[44a] in which are found the standard heats of formation (*i.e.*, the values at 1 atm and at 298 K), the entropies, heat capacities, melting points and boiling points of the elements, their salts, and their oxides. From these data may be computed the heat of reaction, ΔH_r, which, when adjusted for stoichiometry and ambient temperature, is used to determine the heats of reaction of the mixture (Q_r) and the adiabatic reaction temperature. Thermodynamic principles help to determine the selection of reaction candidates and to judge the feasibility of untried reactions.

Whereas thermodynamics describes equilibrium states, thermochemistry covers all thermally induced changes, their kinetics, and their mechanisms (the "reaction paths"). Thermochemistry deals with both magnitude and direction, and predictions of thermochemical effects which require knowledge of the rate of processes, so that time becomes an important variable.

Heat of Reaction

The heat of reaction (ΔH_r) is best calculated from the standard heats of formation of the products and the reactants:

$$\Delta H_r = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants}) \qquad [7\text{-}1]$$

It is important that the state of the reactants be known. This task is facilitated by assuming all reactants to be at the same temperature, such as 298 K. The heats of formation of the reactants from the elements, ΔH_f^{298}, is the reference state for which thermodynamic data are tabulated.[120]

Calculation of the Adiabatic Reaction Temperature

In this calculation only a single equilibrium is considered. In fact, even moderately complex calculations for mixtures of multiple components, especially when these are not present in stoichiometric quantities, cannot be solved by assuming

Table 7-1. Conversion Factors

Units	Multiplication Factors
Heat Capacity, Entropy	
cal/(g-mol·K)	4.187 kJ/(kg-mol·K)
BTU/(lb-mol·R)	1.292 kJ/(kg-mol·K) or 4.187 kJ/3.241(kg-mol·K)
Enthalpy, Free Energy	
kcal/(g-mol)	4.187 MJ/(kg-mol)
kcal/cm^3	4.187 GJ/m^3
BTU/(lb-mol)	2.326 kJ/(kg-mol)
Density	
g/cm^3	$1x10^3$ kg/m^3
lb/in^3	2.768×10^4 kg/m^3
Universal Gas Constant	
1.9864 cal/(g-mol·K)	8.314 kJ/(kg-mol·K)
Pressure	
Atmosphere	1.013×10^5 Pa
Bar	$1 \quad \times10^5$ Pa
Torr (mmHg)	1.333×10^2 Pa
lb/in	6.895×10^3 Pa
N/m^2	1.000 Pa
kgf/m^2*	9.807 Pa
Thermal Conductivity	
cal/ (sec cm^2)(°K/cm)	2.012×10^4 J/sec m °K
W/cm^2 (°K/cm)	0.481×10^4 J/sec m °K
BTU/hr ft^2 (°R/ft)	1.731 J/sec m °K
Mass	
gr (troy, avoirdupois, apothecaries')	0.06481 g
oz (avoirdupois)	28.35 g
oz (troy)	31.10 g
t (short ton)	907.18 kg
t (long ton)	1016 kg
Length	
in	0.0254 m
ft	0.3048 m
mi	1609 m
Explosives Loading	
gr/ft	4.703 g/m
Temperature	
° Centigrade	°C+273.16 °K
° Rankine	1.8 °K (exact)
° Fahrenheit	1.8 °C + 32 (exact)
° Kelvin	(100/180) (°F−32) + 273.16

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* Kilogram force

that the simultaneous equilibria exist in closed form and it becomes necessary to employ either a trial and error computation or an iterative solution of simultaneous equations.

Not long ago, a number of methods were routinely used for the manual calculation of special problems such as the prediction of the composition of rocket exhaust gases. At present, almost all calculations of chemical equilibria are performed by computer and the reader is referred to the specialized literature.[93, 262]

The following is an example of manual calculation of the flame temperature of a magnesium/sodium nitrate composition typical of the kind used in many illuminating flares. There are several possible ways for this reaction to proceed which in turn determine the relative amounts of magnesium and sodium nitrate for a stoichiometric reaction. Two examples are:

$$5\ \mathrm{Mg} + 2\ \mathrm{NaNO_3} \rightarrow 5\ \mathrm{MgO} + \mathrm{Na_2O} + \mathrm{N_2} \qquad [7\text{-}2]$$

$$6\ \mathrm{Mg} + 2\ \mathrm{NaNO_3} \rightarrow 6\ \mathrm{MgO} + 2\ \mathrm{Na} + \mathrm{N_2} \qquad [7\text{-}3]$$

From the JANAF Tables[120] we find that sodium oxide is thermodynamically unstable above 2200 K (*i.e.*, ΔG_f becomes positive). Assuming that the flame temperature is likely to be above 2200 K, it can be concluded that Reaction 7-2 is less likely to occur than Reaction 7-3. From Equation 7-1 the following is calculated:

$$\Delta H_r = [6(-143.8) + 2(0) + 1(0)] - [6(0) + 2(-115.0)] = -632.8\ \mathrm{kcal/mol}$$

This value, calculated for the overall reaction on a molar basis, is equivalent to 2.16 kcal/g.

The above data can be used in a computer solution which tells whether the products are solid, liquid, or gaseous at the reaction temperature, and how much of each product is present at equilibrium, as well as the adiabatic reaction temperature. In a manual computation, the reaction temperature is determined through a trial and error procedure by equating the enthalpies of the reaction products with the heat of reaction:

$$\sum_{T}^{298}(H-H_{298}) + \Delta H_m + \Delta H_b = 632.8\ \mathrm{kcal/mol} \qquad [7\text{-}4]$$

where ΔH_m and ΔH_b are the heats of fusion and of vaporization respectively.

The problem is to determine the temperature at which the equality occurs. The JANAF tables report that magnesium oxide vaporizes at high temperatures and that the vapor pressure is appreciable at its melting point of 3100 K. Therefore, as a first approximation, it can be assumed that the flame temperature is the melting point of the oxide. The enthalpies of the products, as obtained from the JANAF Tables[120], are as follows:

Nitrogen	$(H_{3100}-H_{298})$	... 23.051 kcal/mol
Solid MgO	$(\Delta H_f^{\,3100})$	... 35.847 kcal/mol

for gaseous sodium	ΔH_m	0.622 kcal/mol
	ΔH_b	23.285 kcal/mol
Enthalpy of liquid	$(H_{1100}-H_{298}) = 5.705$	
Enthalpy of vapor	$(H_{3100}-H_{1100}) = 9.993$	
	39.605 kcal/mole	

The total enthalpy of the products at 3100 K, as computed from Equation 7-3, is:

$$(6 \times 35.847) + (2 \times 39.605) + 23.051 = 317.383 \text{ kcal}$$

Because this enthalpy is less than the computed heat of reaction of 632.8 kcal, it can be assumed that the magnesium oxide is molten. Magnesium oxide has a heat of fusion of 18.592 kcal/mole. The revised enthalpy is:

$$(6 \text{ x } 18.592) + 317.383 = 428.935 \text{ kcal}$$

The excess enthalpy (632.8 − 428.935 = 203.9 kcal) is sufficient to vaporize some but not all of the six moles of magnesium oxide, and therefore the original assumption that the combustion temperature did not exceed the boiling point of the oxide was correct. The heat of vaporization of magnesium oxide (133.807 kcal/mol) is the difference between the heat of formation from the elements of gaseous oxide at 3100 K as shown in the JANAF Tables.

Use of Thermodynamic Tables

The two thermodynamic functions of greatest utility in thermochemical calculations are the enthalpy (H) which for isobaric processes equals the heat generated or transferred by a chemical reaction; the other function is the free energy (G) from which the composition at equilibrium and the direction of a chemical reaction can be computed. Only when all products of the reaction are in the condensed phase (as is the case in some pyrotechnic reactions but never in propellant or explosive reactions) is the enthalpy change (ΔH) approximately equal to the free energy change (ΔG). Only in the case of a condensed phase reaction does a negative enthalpy change predict the likelihood of the reaction.

As a matter of convention, enthalpies and free energies are based on a standard state, usually the crystalline solid at 298 K. Also by convention, enthalpies and free energies of formation of the elements in their standard states are zero. Thermodynamic functions with respect to temperature are tabulated in a standard reference.[112] They may also be calculated from the heat capacities and the standard heats of formation. While the equilibria of complex reactions and of multicomponent systems are today most easily calculated by computer, the ability to use tabulated data is a great help in predicting the direction and the extent of the reaction. Although no equilibria depend on the path of the reaction, in analyzing reactive systems, it is necessary to examine the equilibrium under reaction conditions and not at the standard state. For the calculation of the equilibria at high temperatures, information about the stability of the products must be obtained.

Otherwise, the results will be erroneous, as was shown in the preceding example of the flare flame temperature.

Tabulated functions can be used for the prediction of a pyrochemical reaction. For example, should it be desired to find out whether a mixture of carbon and chromic oxide were a useful one, the thermodynamics of the following reaction would be examined:

$$Cr_2O_{3(s)} + 3C_{(s)} \rightarrow 2\ Cr_{(s)} + 3\ CO_{(g)} \qquad [7\text{-}5]$$

There might be a number of other reactions, such as the formation of chromium carbide with excess carbon or the formation of carbon dioxide with excess chromic oxide, or the chromic oxide might be only partially reduced. Of these substances, all, some, or none, might be found in the final reaction product. This is what is meant by a complex equilibrium. Strictly speaking, the following calculation ought to be performed for all possible reactions. The one with the minimum free energy, *i.e.*, the one that is the most negative, is selected as being the most likely.

The free energy change is calculated as follows:

$$\Delta G_T = \Delta H_T - T\Delta S \qquad [7\text{-}6]$$

where ΔG_T represents the value at temperature T and not, as before, at the standard condition. An alternate expression for the free energy equation is:

$$\Delta G_T = \Delta H_f^{298} - T\left(\Delta F_T - \frac{\Delta H_f^{298}}{T}\right) \qquad [7\text{-}7]$$

Note that in Equation 7-5, one product is gaseous so that either Equation 7-6 or 7-7 is used instead of Equation 7-1. The thermodynamic data for the products and for the reactants are as follows:

	$\Delta H_f^{298}\ \frac{\text{kcal}}{\text{mole}}$	$S_f^{298}\ \frac{\text{kcal}}{\text{mole}}$	$\left(\Delta F_T - \frac{\Delta H_f^{298}}{T}\right)\ \frac{\text{kcal}}{\text{mole}}$
Reactants			
Cr_2O_3	−271.2	19.396	19.396
$3C_{(s)}$	0	3 × 1.359	3 × 1.359
Products			
$2Cr_{(s)}$	0	2 × 5.645	2 × 5.645
$3CO_{(g)}$	3 × (−26.417)	3 × 47.214	2 × 47.214
Σ prod − Σ react.	+191.95	+129.459	+129.459

At equilibrium, $\Delta G = 0$. Substituting these values into Equations 7-6 or 7-7, we obtain

$$T = \frac{191950}{129.459} = 1483 \text{ K}$$

We conclude from this that the reaction would not proceed unless the temperature were to exceed 1483 K. Similar calculations for alternate reactions show that even higher temperatures would be required to make this reaction proceed as written. As a candidate for a pyrotechnic reaction this system would be a failure. To determine whether there might be a chance of using this reaction to prepare metallic chromium under a vacuum when the reactants were held at 1300 K the change of free energy with pressure is calculated from

$$\Delta G = -RT \log_e \frac{P_2}{P_1} \qquad [7\text{-}8]$$

Calculating the free energy change from the above data at 1300 K , Equation 7-7 yields:

$$\Delta G = 191{,}950 - (1300 \times 129.459) = 23{,}654 \text{ cal/mole}$$

Setting $P_1 = 1$ atm, from Equation 7-8 it is found that $P_2 = 1\text{x}10^{-4}$ atm, a pressure readily attainable in a laboratory vacuum furnace.

An interesting demonstration of the importance of free energy in determining equilibria is found in the delay mixture of boron and barium chromate. If the heat of reaction at the adiabatic reaction temperature were equal to the free energy change, one would write:

$$2B + 2\,BaCrO_4 \rightarrow B_2O_3 + 2\,BaO + Cr_2O_3 \;\; (4.1 \text{ mass\% B})$$

Experimentally one finds, however, that the maximum heat of reaction is at 14.5 mass% B, because above 1000° C, BO is the stable product instead of B_2O_3. Therefore, the following equation describes the reaction more correctly:

$$4\,B + BaCrO_4 \rightarrow 4\,BO + Ba + Cr$$

At ambient temperature, the reaction products will be a mixture of B_2O_3, BaO, Cr_2O_3 and CrB. If the reaction were accompanied by gas formation, one would expect the propagation rate of this reaction to be pressure dependent. In fact, this is found to be the case when the mixture is prepared mechanically, but not when the mixture is co-precipitated.

Chapter 8

Some Words on Instrumentation

Pyrotechnics, as much as any science, relies on experimentally observed evidence. Significant advances have taken place in recent years in instrumental analysis and measurements.

Heats of Reaction

The preferred tool for measurement of heats of reaction is the bomb calorimeter. The device allows the reaction of a known quantity of substance or mixture in a controlled atmosphere and closed volume. The change of enthalpy (*i.e.*, of heat content) in the bomb is determined by immersion in a bath the initial and final temperature of which are monitored. The heat capacity of the bomb and of the ancillary components is measured by the combustion therein of a known substance (*e.g.*, benzoic acid in oxygen). The calorimeter is allowed to return to standard temperature and pressure in order to account for the heats of vaporization of liquid components. Methods depend on the particular calorimeter used and the reader is urged to follow the manufacturer's instructions. Further details are given by Sumner and Månsson.[231]

The preference in this book is to use the term "reaction" in discussing self-contained phenomena and to reserve the word "combustion" for processes which involve the ambient atmosphere (*e.g.*, the "combustion" of magnesium in air or chlorine, but "reaction" of magnesium with potassium perchlorate).

Currently the most popular tool in the study of pyrotechnic phenomena and reaction kinetics is differential thermal analysis (DTA). This is, for all practical purposes, the same as differential scanning calorimetry (DSC). This method involves the measurement of the difference in temperature (ΔT) between the sample and a reference material which has no thermal transition in the temperature region of interest. This reference material may be inert or it may be a thermally insulated calorimeter. The temperature of the calorimeter is changed in a programmed manner. A valuable adjunct in this work is a microprocessor. This permits the control of temperature ramps, records, differentiates, and stores the data, as well as identifying maxima and minima. The thermocouples (or thermistors) which are located in the sample and in the reference material are wired back-to-back so that if the two junctions are at the same temperature, the resulting electromotive force is zero. Normally, the amplifier and the recorder are wired so that a higher sample temperature is displayed by a higher voltage. The allowable temperature range is limited only by the design of the calorimeter and the thermocouple device. In an inert atmosphere or a vacuum, temperatures of 2400° C are attainable.

Endotherms are associated with phase transitions and reduced heat capacity (sometimes due to sample loss) and exotherms signal heat generation. The deflection of the recorder is related to the rate of heat generation (in µw) by a factor that can be obtained by calibration with a reference material or from the manufacturer's data. The maxima in the exotherms are dependent on the rate of heating and are a measure of the kinetics of the reaction. Dependable kinetic data can be obtained only with a series of isothermal runs. The peculiar experimental conditions of a DTA experiment would seem to be rather remote from the "real world" and therefore the data obtained would have little resemblance to data which might be obtained from a bulk sample. Nevertheless, DTA is a popular technique in safety studies because the onset of decomposition or reaction is clearly signaled even for very small quantities (1-10 mg), and because the atmospheric conditions can be controlled independently.

Kinetics of Reaction

Two studies have been reported on the determination of kinetic parameters for a reaction in a single DTA run[130, 261] by the integration of the equation:

$$\frac{dx}{dt} = A(1-x)^n, \text{ where the exponent } n = \frac{-E_a}{\mathrm{RT}} \qquad [8\text{-}1]$$

By equating the reaction rate, *dx/dt*, with the rate of change of the temperature, *dT/dt*, and assuming that the order of the rate law, n, and the activation energy, E_a, remain constant, all parameters can be computed from two or more data points on a single run.

Accelerating Rate Calorimetry

A newer technique for the study of exothermic reactions is Accelerating Rate Calorimetry (ARC™).* Here the sample (1-10g) is contained in an explosion-proof container where it is heated in a stepwise fashion. As soon as a thermal sensor detects heat generated from the sample, the experiment is allowed to progress under strict adiabatic control.[224] A microprocessor displays the rate of self-heating as a function of temperature. The slope of the curve is related to the activation energy and the reaction-rate constant of the process. Another important datum is the time taken to attain maximum reaction rate. This has been successfully applied to real-life hazard prediction.[238] For instance, from the thermal constants of the containers, an estimate of the safe life of the system can be made as a function of its mass. Analogous data are generated for gas-forming reactions in terms of rate of pressure generation, thus providing full time, temperature, and pressure data in one experiment.

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* ARC™ is a registered trademark of the Columbia Scientific Industries Corporation, P.O. Box 9908, Austin TX 78766.

Whereas the time required per run can be lengthy (twenty-four hours is typical), many of the data obtained are unique in that they do not depend on the quantity of material tested. Therefore, critical storage masses and critical storage temperatures are accessible from a single run in a reasonable time frame. Runs in controlled atmospheres are also possible.

An application of ARC™ to a strictly pyrotechnic problem involved a study of the stability of titanium subhydride when it is mixed with potassium perchlorate.[79] Because ARC™ should only be applied to reactions which go to completion below 500° C, the high-temperature stability of the titanium subhydride mixture limited the interpretation of the data

In an unpublished study of the decomposition of black powder,* useful ARC™ data were obtained which indicated that ARC™ is of value in such pyrotechnic reactions in which the reaction temperature falls within the operating range of the instrument. For instance, Fig. 8-1 shows the time to maximum rate as a function of temperature. From these data if could be inferred that given a mass of black powder thermally insulated, stored at 180° C, 500 minutes would elapse prior to initiation, but at 240° C only 13 minutes would.

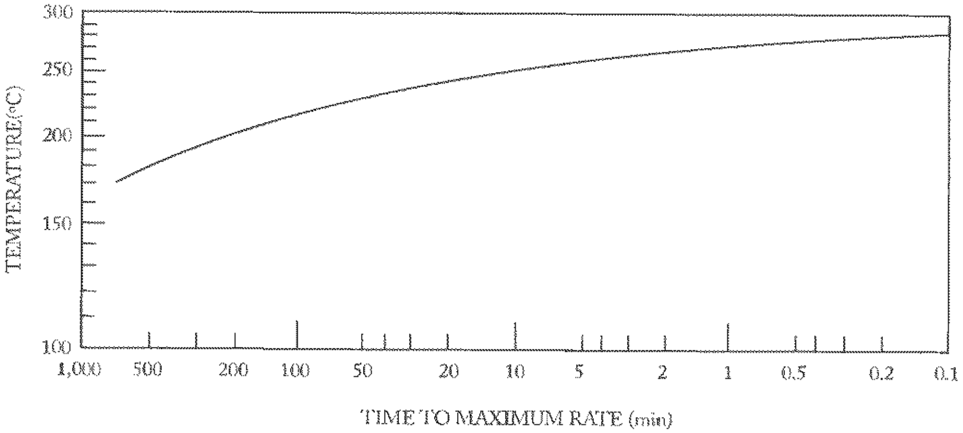

Figure 8-1. Time to ignition of black powder as obtained by ARC™.

Thermo-Gravimetric Analysis

Commercial devices for thermogravimetric analysis (TGA) have become "user friendly". The onset of reactions and the differentiation between phase changes (no mass loss) and reaction with mass loss or gain can be observed, and so can be distinguished from observations with DTA. The mass loss rates, preferably obtained from isothermal runs, lend themselves directly to kinetic analysis:

$$\frac{dw}{dt} = Am^{n} \text{ where the exponent } n = \left(\frac{-E_a}{RT}\right) \qquad [8\text{-}2]$$

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* Courtesy Dr. T. T. Griffiths, RARDE, Fort Halstead, Sevenoaks, Kent, UK

Determination of the rate of mass change at several temperatures permits computer-programmed curve fitting and calculation of the activation prefix A, the activation energy E_a and the order of the reaction, n, with high precision over a wide portion of the thermogram.

These various techniques, DSC, DTA, ARC™, and TGA all complement each other and aid in the study of the thermal stability and thermal initiation of many kinds of pyrotechnic mixtures. The techniques recommend themselves because the quantities of materials studied are usually small, so that safety in laboratory operation and preservation of the laboratory equipment are greatly facilitated. On the other hand, it is necessary to guard against non-homogeneity in the sampling of the lot. Multiple and consecutive reactions can be studied at times if mechanistic explanations exist. Conversely, the observation of multiple and consecutive reactions frequently aids in the establishment of a reaction mechanism. Much of the mystery of the pre-induction step is frequently removed by a preliminary precision thermal analysis. For instance, if the reaction is preceded by melting, or if the reaction is characterized by a phase change, erroneous kinetic data are often obtained, because the order of a reaction has no real significance in such cases. Likewise, autocatalysts may lead to profound errors in interpretation.

Mass spectroscopy, performed on the starting materials or on the products of thermal analysis, helps to identify the role of trace contaminants in affecting the kinetics of a process. For instance, this author[102] showed by means of mass spectrometry that the effectiveness of antimony sulfide in influencing the "quickness" of a pyrotechnic mixture depended greatly on the amount of sulfur contamination in the sample. Furthermore, mass spectrometry coupled with thermal analysis can explain the reaction mechanism by identifying the change of composition of the gaseous reaction products with temperature.

Temperature Measurement

Pyrometry

Pyrotechnic reactions take place at high temperatures, at relatively high rates, and with the formation of copious smoke and gas. The problem of temperature measurement is thus fraught with difficulty. This discussion can only touch on the complications without really helping the reader to solve specific problems.

Temperature measurement by pyrometry and radiometry is possible because radiation emitted by a luminous solid is a function of its temperature. A radiometer, or pyrometer, is an optical instrument which collects radiation from a narrow field of view and converts it into an electrical signal. The magnitude of this signal can be measured with great precision and speed.

The energy radiated by a body covers a wide range of frequencies and wavelengths. The wavelength at which the maximum or peak radiation occurs, is determined by the temperature of the body. As the temperature increases, the peak radiation shifts to the shorter wavelengths and the total amount of radiated energy increases.

The ideal source, and the only one for which the total radiated energy is a simple function of temperature, is called a "black body." In pyrotechnics, however, the radiating body does not radiate over the entire frequency range in a uniform manner because the emittance of the radiator changes with frequency (*i.e.*, temperature). A body the emittance of which is relatively independent of temperature, but less than that of a black body, is called a grey body.

In order to minimize the errors inherent in the grey body assumption, pyrometry is not usually performed with wide frequency band radiometry, but with pyrometers which filter the observed radiant energy to narrow bandwidths. Emittance can be determined at the wavelength of interest with reflectance spectrophotometry (*i.e.*, by measuring the reflected energy with a monochromator). Pyrometers operate as "brightness pyrometers"; usually at 650 nm. They are accurate only if the emitter is grey or black at this wavelength. In some experimental set-ups it is possible to form a cavity into the surface which can then be considered "black" and for which no emittance correction is necessary. The pyrometer is usually so configured that the surface, and a heated filament which acts as an internal standard, are viewed alternately. The rate of switching is called the "chopping rate" which ultimately limits the temporal data resolution and which therefore limits the time frame in which kinetic data can be acquired.

An alternate type is a "two-color pyrometer" which is designed to eliminate the need for emittance corrections by measuring the ratio of the radiant energy at two narrow wavelength bands. Emissivities will cancel only if the source has the same emissivity at both wavelengths (*i.e.*, is a grey body). Because emissivity changes with temperature, the accuracy of a two-color pyrometer decreases with increasing temperature.

In pyrometry, the size of the source must at least equal the size of the detector (the "spot"). The duration of the event must at least equal the exposure time of the detector, *i.e.*, the interval between "chops" of an AC instrument. Readings will be low when the radiation must pass through a colder intervening gas envelope, or when it is partially obscured by smoke. The reader is directed to the voluminous special literature on this subject.[30]

Flame Temperatures

The line reversal method is the most favored technique for the flame temperature range from 1500-5000 K.[88, 229] Unfortunately, the technique requires complex apparatus and is therefore better suited for laboratory studies as opposed to field studies.

This line reversal method is based on the use of emitters present in the flame, or which are introduced into the flame, and which emit characteristic spectral lines. The process employed is to determine the point of reversal. This point corresponds to the instant at which the radiation emitted by the filament at a known temperature is made to pass through a flame at the same temperature so that the absorption is compensated by the emission from the flame. This causes the flame to vanish. At any other temperature, the filament will either appear to be luminous or as a dark line. Flame temperatures which exceed the filament temperature may be attenuated by the use of filters. The absorbance of the filter being known, it becomes possible to determine the brightness temperature of the flame, the true temperature of the filament, and the absorbance of the flame. Assuming the temperature of the filament to be known and constant, simultaneous readings of the radiant output of the flame with and without the filament permit temperature resolution in the time frame of the chopper.

Thermocouple Thermometry

Thermocouples have many advantages in pyrotechnic studies, not the least being that they are inexpensive, and therefore expendable. Thermocouples can be used over a wide range of temperatures from subambient to 2100° C. The number of potential thermocouple combinations is virtually infinite but fortunately there has been a large amount of standardization. Finally, thermocouple systems are easy to instrument: portable potentiometers, recording potentiometers, galvanometers, and oscilloscopes are all commonly used. There is, for high temperature measurements, no real need for a temperature-compensated junction. The feature this author likes best is that in a sacrificial application, multiple thermocouples give a measure both of the rate of propagation of the reaction, and of the ignition temperature. Thermocouple response is not linear over wide temperature ranges, and for precise work, each thermocouple (from each batch of wire) should be calibrated using the freezing points of a series of pure metals. The electromotive force values for the various couples are tabulated in various handbooks and in the trade literature generously supplied by the manufacturers of the wires.[28]

Table 8-1. Thermocouple Combinations

Type Designation*	Temperature Range, °C	Materials
B	0 to 1820	Platinum-30% Rhodium *vs.* Platinum-6% Rhodium
E	−270 to 1000	Nickel-Chromium Alloy *vs.* Copper-Nickel Alloy
J†	−210 to 1200	Iron *vs.* Copper-Nickel Alloy
K	−50 to 1767	Platinum-13% Rhodium *vs.* Platinum
R	−50 to 1767	Platinum-10% Rhodium *vs.* Platinum
	up to 2100	Tungsten-3% Rhenium *vs.* Tungsten-25% Rhenium in Argon, Hydrogen or Vacuum

* The letter type designates the thermoelectric properties, not the precise chemical composition. Thermocouples of a given type may have variations in composition as long as the resultant thermoelectric properties remain within the established limits of error.

† The negative thermoelement for Type J thermocouple is a copper-nickel alloy known ambiguously as constantan, referring to anything from 45-60% copper content.

Measurement of Electrostatic Sensitivity

This discussion of the measurement of electrostatic sensitivity was obtained to a large extent from Kirschenbaum's article, who applied his finding mainly to the response of lead azide.[74] His conclusions apply, generally, to the interpretation of other electrostatic sensitivity data. Another study is that of Perkins.[185] Wang *et al.*[246] compared static sensitivities of Ti, Zr/$KClO_4$ systems.

The usual method for measuring the minimum initiation energy of a material is to subject it to a single discharge from a standard capacitor. The capacitance or the voltage across the capacitor is reduced until no initiation occurs (see Chapter 4 on the up-and-down method). The energy is the calculated as $e = 0.5\ CV^2$. By this technique energy values varying by 8 orders of magnitude have been reported for a single substance when the data were obtained from different sources, each using different conditions or apparatus.

The impedance of the capacitive circuit and the spark gap geometry affect the rate of energy delivery and thus the length of the spark. Also, the mechanism of initiation is important, whether it is an electronic process (as in primary explosives) or one where the electrostatic energy must first degrade to thermal energy (as is typical for pyrotechnic mixtures). There are no standard electrostatic sensitivity tests. The two most common are fixed-gap method and the approaching-electrode method.

In the fixed-gap method, two electrodes are placed at a fixed distance, the electrode configuration being a needle-plane, a sphere-plane, or parallel planes. The capacitor, having been charged to a known voltage, is discharged across a low impedance switch.

In the approaching-electrode method there is no switch. Initially, the gap is made too wide for a gaseous discharge to take place. The threshold for the gap breakdown is governed by Paschen's Law which states that the breakdown voltage is dependent on the product of the gas density and the distance between the electrodes. In air, the breakdown voltage is about 300 V.

A capacitor can discharge by an arc discharge or by a spark discharge, both of which may occur in a single event. An arc discharge is characterized by a low voltage drop across the gap (30-60 V) and high currents (0.3-0.5 A). A spark discharge is maintained by secondary emission of electrons from the cathode. The voltage drop is 300-400 V and the current is in the milliampere range. The effect of the impedance of the circuit-gap system on initiation energy is to produce a minimum initiation energy. This phenomenon was illustrated in a series of tests on lead azide[74] in which the storage capacitor was kept constant at 2800 pF and by varying the RC time constant of the circuit from 0.1 μs to 40 ms by increasing the series resistance from 1 Ω to 15 MΩ. The energy was shown to decrease from $8x10^{-3}$ J to a minimum of 6.5×10^{-4} J at about 1 ms and then to increase again to 1.4×10^{-3} J as the RC time constant increased to 43 ms. Rather than giving ranges of values, the minimum initiation energy should be cited.

For all pyrotechnic devices adequate closure and grounding is essential to minimize the effect of static discharge. Material in a closed and conductive container is said to be in a Faraday cage, experiencing no charge effects. Extensive tabulations of electrostatic hazard data are available.[74, 185]

Chapter 9

Ignition

> *And Samson went and caught three hundred foxes and took firebrands, and turned tail to tail, and put a firebrand in the midst between two tails.*
>
> *And when he had set the brands on fire, he let them go into the standing corn of the Philistines, and burnt up both the shocks, and also the standing corn, with the vineyards and olives.*
>
> JUDGES xv:4, 5 (*ca.* 1000 B.C.)

We are not sure what improvements have taken place in recent years in the relationship between the Israelites and their neighbors, but we do know that effective ignition remains a current problem in pyrotechnics. In many ways, pyrotechnics has the edge over its sister disciplines in that it provides prime ignition – *i.e.*, the translation of a mechanical motion, an electrical signal, or a chemical action into flame or detonation; or conversely, turns a pyrotechnic event back into kinetic work. The association between fire and the sword has always been a close one, but pyrotechnic ignition more often serves a utilitarian or æsthetic purpose. Ignition and its applications are of such diverse nature that they must be divided into several categories, which are treated in Chapters 9–14:

Ignition Theories
Autoöxidation – Self-ignition – Hypergolicity
Matches
Primers and Ignition Mixtures
Shock Initiation – Laser Ignition

Ignition

Initiation of pyrotechnic reactions continues to be a much-explored but little-understood subject. Ignition requirements can only be estimated because so many factors entering into an understanding are obscured by the complexity of the chemistry of heterogeneous solid mixtures. Even so fundamental a process as ignition by spark (from a flame carrier or static discharge) has not been analyzed successfully. All that can be done at present is to examine the fundamental relationships as an aid in correlating data.

In contrast with pyrotechnics, the initiation requirements of explosives are quite well understood. Although the mechanism of explosive initiation is not necessarily applicable to pyrotechnics, it is a useful first approximation. Chapter 13 will discuss some pyrotechnic devices to which such principles have been successfully applied.

Initiation of a pyrotechnic reaction is a transient event. In thermal ignition, temperature is a function of both time and position. Therefore, a mathematical model requires the solution of nonlinear, partial differential equations. Such solutions are not available explicitly, and computers are used to calculate close approximations to the hypothesized model. As an illustration, a simplified model follows.

Ignition at Constant Heat Flow

Let the ignition process take place in a planar geometry, dependent only on thermal transport. Assume that the duration of the heat pulse is long compared with the time required for ignition. Also assume that reaction occurs to a negligible extent during ignition so that it may be described by a zero-order rate law. All transport and thermal properties remain constant throughout the process. Finally, assume that the surface temperature is known and remains constant. The following is the general expression for heat transport in a solid during a chemical reaction:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + \left(\frac{Q}{C\rho}\right) A_o^{\left(\frac{-E_a}{RT}\right)} \qquad \textbf{[9-1]}$$

T = temperature, °K
Q = heat of reaction, cal/g
C = heat capacity, cal/g °K
t = time, s
A_o = pre-exponential factor, s^{-1}
E_a = activation energy, cal/mol
R = gas constant, cal/mol °K
α = thermal diffusivity, cm^2/s
ρ = density, g/cm^3
λ = thermal conductivity, cal/cm s °K

Subscripts:
o = starting

Typical magnitudes for the variables are:

O = 500-1000 cal/g
A_o = 10^{12}-10^{15} s^{-1}
λ = 0.2-0.002 cal/cm s °K
C = 0.1-0.3 cal/g °K
E_a = 30-80 kcal/mol
ρ = 2-6 g/cm^3

Note that while constancy of the material properties is usually assumed, in reality abrupt changes in transport and kinetic parameters are observed on ignition. Solutions to Equation 9-1 are therefore at best a guide to the understanding of the process and do not take the place of experimental measurements.

Merzhanov and Averson[166] have shown that for this idealized case, the time required for ignition is:

$$t_i = \left[\frac{RT_o^2}{E_a}\right]\left(\frac{C}{\rho\, QA_o}\right)^{\left(\frac{-E_a}{\mathrm{RT}_o}\right)} \qquad [9\text{-}2]$$

Subscript:
i = ignition
o = starting

Usually, the surface temperature (T_o), as in convective heat transfer, is not known, and a characteristic temperature is chosen. One might select the ignition temperature obtained, for instance, by DTA. The ignition temperature of a pyrotechnic mixture is by no means a fixed value but depends on atmospheric pressure and composition, trace contaminants, particle size, stoichiometry, heating rate and heat losses. Yet, most thermal transport studies are not greatly dependent on the characteristic temperature. For this reason, an approximate ignition temperature produces results which are no worse than those obtained by more rigorous methods. For the case of an unknown surface temperature, Merzhanov recommends the following expression for the ignition time:

$$t_i = 0.46\, C\rho\lambda\,(T_i - T_o)^2\left[1+\frac{[12\,RT_i^2]}{[\mathrm{E}(T_i-T_o)]}\right]\left(\lambda\frac{dT}{dx}\right)^{-2} \qquad [9\text{-}3]$$

where $\left(\lambda\frac{dT}{dx}\right)$ is the heat flux (cal/cm^2 s) across the surface and is assumed to be constant.

Merzhanov and Averson[166] define for the heat flux, a critical condition where ignition takes place when the heat gained by the surface equals the heat from the pyrotechnic reaction. For cases where no reaction occurs and for which the temperature is therefore maximum at the surface, the expression for the heat flux has the following appearance.

$$\left[\lambda\left(\frac{dT}{dx}\right)\right]^2 = \lambda\left(\frac{RT_i^2QA_o}{\mathrm{E}}\right)^n \qquad [9\text{-}4]$$

where $n = \left(\frac{-E_a}{\mathrm{RT}_i}\right)$.

The width of the chemical reaction zone at the point of ignition is given by

$$X_i = \sqrt{\frac{(RT_i^2\lambda)}{[EQ\,\rho\,A_o]^n}} \qquad [9\text{-}5]$$

where $n = \left(\frac{-E_a}{\mathrm{RT}_i}\right)$.

This equation was first derived by Frank-Kamenetski[84] for the thermal ignition of a homogeneous explosive. The ignition temperature (called the "critical temperature" by Frank-Kamenetski) is therefore

$$T_i = \frac{\mathrm{R}}{\mathrm{E}\log_e\left(\frac{QEX_i^2\,\rho\,A_o}{\lambda\,RT_i^2}\right)} \qquad [9\text{-}6]$$

Ignition by a Point Source

When the heat source is small (*e.g.*, a hot wire), one-dimensionality can no longer be assumed, and Equation 9-1 is then written with a cylindrical or spherical coordinate system.

However many special solutions for special ignition problems have been devised, there are really no good data for pyrotechnic systems which might be used to test the equations. Frank-Kamenetski expressions have been applied successfully to explosive systems, and Merzhanov[166] discusses data obtained on nitrocellulose.

Dynamic Ignition Pulse

Whenever the heat source ceases before ignition commences, it is referred to as a dynamic ignition pulse. Examples of this are ignition by a squib or a laser pulse, by spark, by shock or by impact. Dynamic ignition is the regime which is most typical of pyrotechnic ignition and at the same time, the one least understood. In these cases, the surface temperature drops after the heat pulse, ignition delay is increased, and the assumption of zero-order chemical reaction in the hot zone is no longer valid. Thermal transport phenomena then become so complex that the system cannot, at present, be described by a simple model.

One example is the heating of a semitransparent substance by radiant energy flow (as in laser ignition). Merzhanov[166] gives an expression for the required energy flux in terms of the absorption coefficient of the mixture. The general experience has been that, for pyrotechnic systems, the absorption coefficient and the activation energies are so high that the kinetic terms in the Frank-Kamenetski treatment dominate, making the Frank-Kamenetski analysis quite insensitive to small changes in property values. As long as the heating rates are high, ignition temperatures may be chosen arbitrarily (for instance, as determined by DTA), even though the ignition temperature in a dynamic ignition is higher than one would measure by the conventional auto-ignition temperature determination.

The difficulties in dynamic ignition may justify an empirical treatment. Consider the required enthalpy rise to assure ignition of the heated zone, as given by Equation 9-5. Correlation of this heat with, *e.g.*, the enthalpy of sparks or the heat of a squib, will show the direction required in formulation or configuration of improved devices. Limited success has been reported for a similar approach to shock initiation (Chapter 13) and to hot spots analysis of explosives.[169]

Chapter 10

Primary Ignition

Autoöxidation – Self-Ignition

The intriguing subject of primary ignition is in large part the study of a large and diverse group of suitable chemical substances. Self-ignition may, of course (as is the case with primary explosives), be triggered by heat, friction, or shock alone, or it may be brought about by the action of the environment, by moisture, air, or some other trigger. It is this latter group of materials which we shall stress first.

The mechanism of autoöxidation is always a complex one involving both mass transport of the reactant (air or moisture) and the kinetics of the chemical action which is accelerated, in the absence of heat loss, until the ignition temperature is reached. The ignition temperature itself is not an intrinsic property of the substance, but is a reflection of the processes occurring. Strictly speaking, any combustible substance could be made self-igniting if one were to heat it sufficiently, shock it hard enough, or grind it fine enough. The special interest of auto-ignition attaches itself generally to those substances which have this property at room temperature, and these are discussed here.

The substance which most readily comes to mind is white phosphorus. Though not of great importance in pyrotechnics, historically it has played an important part in ignition systems. It may self-ignite in air at temperatures as low as 16° C if access to air is partially restricted by covering the surface with cotton, sulfur, resin, or charcoal[70]. White phosphorus is readily dissolved in carbon disulfide, and the solution may then be used as an incendiary agent.* The ignition may be retarded by diluting the carbon disulfide with a volatile hydrocarbon.

Because of its ease of ignition, white phosphorus is kept (and best manipulated) under water. It may ignite in air by the friction caused when cut with a knife, and most assuredly, when dispersed by an explosive charge. Burning phosphorus, after being doused with water, will reignite spontaneously after drying. This is also true of red phosphorus because during its burning some will volatilize and recondense in the white allotropic form. White phosphorus is toxic (see Chapter

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* This is the legendary "Fenian Fire" used by the Molly Maguires in their depredations connected with Pennsylvania labor disputes during the late nineteenth century.

11 on the history of matches), and contact with the skin while burning will produce deep and painful lesions. The white fumes are phosphorus pentoxide and have found application as artificial fog (see Chapter 20 on Smoke), although now superseded for most applications.

The spontaneous ignition of white phosphorus in air can be made more reliable when an eutectic mixture (m.p. 40° C) of 55% white phosphorus with 45% of phosphorus sesquisulfide (P_4S_3) is used[70]. Sulfur will also form such an eutectic (m.p. −7° C) but its ignition characteristics have not been reported.

Phosphines, silanes, and boranes are the hydrides of their respective parent elements. Of these, the phosphines are of special interest because they can be prepared by reacting metallic phosphides with water:

$$Ca_3P_2 + 6\ H_2O \rightarrow 3\ Ca(OH)_2 + 2\ PH_3$$

The major product of the above reaction is diphosphine, P_2H_4, which is the active agent in the Marine Location Marker (night)[70]. A large amount of calcium carbide (CaC_2) produces, on contact with water, acetylene, for which the calcium phosphide furnishes the ignition agent.

Silanes, produced by the action of acids on metallic silicides, have not found practical application in pyrotechnics. Boranes have excited considerable interest as potential high-energy propellants, but to date they are not more than theoretical candidates. Boranes were traditionally prepared from lithium borohydride. This author has synthesized diborane, B_2H_6, by the action of hydrogen chloride on boron carbide at 1000° C. A byproduct is chloroborane, BH_2Cl, which makes the borane self-igniting in air. Diborane, upon pyrolysis, yields the higher boranes, namely tetraborane, pentaborane, and decaborane. These compounds can be readily alkylated to form liquids or reacted with amines to form solids which are somewhat more stable than their parent compounds. All react with water or alcohol, with which they form hydrogen, which becomes self-igniting. It is a memorable experience to see a vacuum line light up like a neon light just before the explosion.

Phosphines, silanes, and boranes are highly toxic and inhibit liver function. A special word of caution is expressed regarding these and the compounds discussed below.

Sodium hydride, NaH,[70] is stable in dry air, but may ignite in moist air. Metallic sodium should be stored under a hydrocarbon, but *never* in a chlorinated hydrocarbon, with which it may react explosively. The classic example is the reaction of metallic sodium with chloroform, exploding with a bright flash:

$$6\ CHCl_3 + 6\ Na \rightarrow 6\ NaCl + 6\ HCl + C_6Cl_6$$

Similarly, potassium hydride has been reported to burn in air[70]. Beryllium, lithium, and aluminum borohydrides are also spontaneously flammable in air, as are the hydrides of uranium, cerium, and thorium[62]. Compounds of these metals with alkyl or aryl groups are spontaneously flammable in air, especially the methyl and ethyl compounds. Similarly active are alloys of the alkali metals with aluminum, zinc, and arsenic.

Beryllium and magnesium alkyls react not only with air and carbon dioxide, but also with water and carbon tetrachloride. However impractical metal alkyls may be for pyrotechnics, their potential use as fuel additives make them an interesting group of compounds. Table 10-1 is a tabulation of spontaneously ignitable metal-organic compounds, updated using Douda's report[62].

The reactive nature of the alkali metals, and the need to store them under hydrocarbons, has been briefly discussed. Lithium exhibits behavior in many ways more like the Group II element, magnesium, than like sodium, exhibiting the well-known phenomenon, which occurs among the lighter elements, of "diagonal relationships." In this case, it is because a protective coating of lithium hydroxide builds up on its surface. This not only protects it from further attack, but even allows it to be used as an anode in an aqueous electrolytic cell provided that the electrolyte is alkaline.

Sodium forms an eutectic with 77.2% potassium, melting at −12.3° C. This liquid alloy, perhaps because of its quickly renewing surface, ignites spontaneously, especially when dropped on the floor. Few of these elements can be considered suitable by themselves for pyrotechnic purposes on account of their tendency to self-ignite. Some are mentioned here for no other reason than to highlight the potential risks inherent when they are processed.

Nickel can be converted into a sponge called *Raney nickel*, which is used as a catalyst in the hydrogenation of organic compounds. It is made by alloying nickel with aluminum and removing the aluminum by dissolving it with a caustic. The residual spongy nickel must be kept under water or a hydrocarbon because it bursts into flame when it is dry. Care must be taken not to blend this aqueous slurry with aluminum, because on drying, the mixture ignites through the highly exothermic formation of the intermetallic alloy nickel aluminide. Activated metal surfaces are of special interest for use in decoys, in which the metals are configured as thin foils[10]. When nickel is deposited electrolytically on a mercury cathode, the amalgam appears to contain up to 24% nickel. When the mercury is distilled off, pyrophoric nickel is left behind. Nickel, iron, and cobalt can be rendered pyrophoric by first alloying with zinc, then distilling off the zinc. The rare earths and the actinides can be made pyrophoric by alloying. This means that iron alloys of mischmetal and of depleted uranium become pyrophoric fragment generators in certain incendiary ordnance devices when they are dispersed. It is preferable to use the term "pyrophoric" when ignition occurs on exposure to air, and to exclude those cases where the metal is merely a spark generator when abraded. Cerium, for example, is a prodigious producer of white-hot sparks when scratched, abraded, or struck with a hammer.

Pyrophoricity

The matter of pyrophoricity is of particular interest in the formation of sparks whether these be employed in commercial products such as cigarette lighters or in incendiary munitions. The classification of metals according to their tendency to spark profusely when ground, abraded, or fragmented has been much studied.

Table 10-1. Spontaneously Ignitable Metal-Organic Compounds

Compound *(For references see bottom of Table)*	**m.p. (°C)**	**b.p. (°C)**	**Remarks**
$LiCH_3 - LiC_3H_7$			burn with red flames
NaC_xH_y*			burns with declining vigor as *x* (of C_x) increases chain length
K, Rb, Cs alkyls			increasing flammability with increasing atomic weight of metal
$Be(C_xH_y)_2$	approx. −13		sublimes *in vacuo*; flames in CO_2
$Mg(CH_3)_2$			higher alkyls are more active, explosive in water, glow in CO_2
$Zn(CH_3)_2$	−40	46	burns with blue flame, higher alkyls less flammable
$Cd(CH_3)_2$			ignites on paper
$B(CH_3)_3$	−161.5	−20	
$B(C_2H_5)_3$	−93	95	burns with green sooty flame
$B(C_4H_{10})_3$	−34	170	alkyl boranes reduce the ignition temperature of jet fuel
BH_3BrAs (d)	7	40	
$(C_2H_5)_3B_2H_3$ (d)			
B_2H_5Cl	−142	0	halogenated boranes generally burn spontaneously in air
$B(C_6H_{14})Cl$ (a)	<125	127	
$B(C_6H_{15})$ (b)	−93	95	
BH_3Br_3P (c)			
$Al(CH_3)_3$	15	122	
its ether complexes	−30	159	
$Al(C_2H_5)_3$ - $Al(C_xH_y)_3$	46-196+	194+	decompose in air, flame with water

Compound *(For references see bottom of Table)*	**m.p. (°C)**	**b.p. (°C)**	**Remarks**
Al $(C_2H_5)Cl_2$	22	194	
$Al(C_4H_{10})Cl$ (e)	−74	208	
$Al_2C_3H_9Br_3$ (f)	4	166	
$Al(BH_4)_3$			
$Ga(CH_3)_3$	−15.8	55.7	ignites at 76° C, explosive in air at room temperature
$Ga(C_2H_5)_3$	−82.3	142.6	ignites in air with a purple flame
$Tl(CH_3)_3$	38.5		
$PH_x(C_yH_z)_n$		−14 to 128	explosive in air; paper soaked in phosphines flames when exposed to air
$HAs(CH_3)(C_2H_5)$		71	
$(H_3C)_2As\text{-}As(CH_3)_2$	−6	165	cacodyl, all arsenous compounds are extremely poisonous and malodorous.
$Sb(C_xH_y)_3$		80.6+	ignites on filter paper
$In(C_2H_5)_3$	−32	144	
$In(CH_3)_3$	−88.4	136	
P_2H_4			
$Bi(C_xH_y)_3$		approx. 110	explodes on being heated in air
$Te(C_2H_5)_2$	138		toxic

* Subscripts *x*, *y*, ...*n* stand for integers, 1 ...*n*

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b. *Acta Chem. Scand.*, Vol. 8, p. 1799 (1954)
c. *Chem. Rev.*, Vol. 42, (1942)
d. *J. Chem. Phys.*, Vol. 8, p. 188 (1940)
e. *Ann. Chim.* (Rome), Vol. 48, pp. 193-7 (1958)
f. Ethyl Corp. *Bulletin*, "Aluminum Alkyls," Dec. 1958

Table 10-2. Empirical Pyrophoricity Determination

Metal	Free Energy of Oxide Formation kJ/mol/O atom	Oxide Volume/ Metal Volume	+ Pyrophoric ? Borderline − Not Pyrophoric	Electron Configuration
U	−535.9	3.10	+	6*d*1 7*s*1
Th	−586.6	1.36	+	6*d*2 7*s*2
Zr	−511.6	1.55	+	4*d*2 5*s*2
Hf	−576.5	1.62	+	5*d*2 6*s*2
Ce	−485.6	1.23	+	5*d*0 6*s*2
La	−640.6	1.11	+	5*d*1 6*s*2
Pr	−620.5	1.12	+	5*d*0 6*s*2
Nd	−616.7	1.12	+	5*d*0 6*s*2
Sm	−431.2	1.06	+	5*d*0 6*s*2
Y	−427.0	1.44	+	4*d*1 5*s*2
Ti	−426.6	1.78	+	3*d*2 4*s*2
Be	−582.0	2.77	+	— 2*s*2
Al	−525.9	1.28	?	— 3*p*1
Cr	−272.1	3.92	?	3*d*5 4*s*1
Co	−216.5	2.10	?	3*d*7 4*s*2
Pb	−188.0	1.31	?	5*d*10 6*p*2
Ni	−211.9	1.68	?	3*d*8 4*s*2
Fe	−245.3	2.06	?	3*d*6 4*s*2
Mn	−363.0	2.07	?	3*d*5 4*s*2
Ca	−604.6	0.83	—	3*d*0 4*s*2
Mg	−569.8	0.84	—	— 3*s*2
Sr	−560.2	0.69	—	— 5*s*2
Li	−596.2	0.60	—	— 2*s*1
Na	−376.8	0.32	—	— 3*s*1
K	−319.5	0.51	—	— 4*s*1

Hillstrom[113] examined the question of which metals would so ignite in air. He found empirically that the spontaneous reactivity of the metal with air is related to the ratio of oxide volume to metal volume,* as well as the free energy of oxidation. The free energy of oxidation is the measure of the thermodynamic driving force while the high oxide volume is seen as the cause of "popcorning," which is believed to be characteristic of pyrophoric metals.

Some elements, such as aluminum, possess the desired properties but in fact fail to burn spontaneously, except as a sub-micron powder. Hardness as a criterion for pyrophoricity has found application only in the study of the sparking characteristics of mischmetal and similar products. Hillstrom set the threshold for the free energy of formation at 400 kJ/mol for each oxygen atom, and found that the volume ratio of oxide to metal must exceed one.

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* An idea originally identified as the "Pilling-Bedworth ratio."

In borderline cases, the particle size and the surface conditions play a decisive rôle. Table 10-2 lists the pyrophoric elements together with their relevant properties. Those which are borderline cases have been labeled with a question mark.

In addition to the primary meaning of pyrophoricity as autoignition in air, a secondary one pertains to the production of sparks when the material is ground or abraded. The classic method of fire generation by the striking of flint on steel produces "cool" sparks which may ignite certain carbonaceous solids (such as loose cotton or tow) but usually not liquids (such as diesel oil).

Hotter sparks are produced by abrasion of the rare earth metals and of the actinides. Table 10-2 shows the values of ΔG^0 for these and other elements, showing their correlation with observed pyrophoricity. In fact, the basis for spark-producing "flints" as used in pocket lighters is mischmetal, a naturally occurring mixture of lanthanides, consisting of 50% cerium, 25% lanthanum, 16% neodymium and smaller amounts of the other rare earth metals. Mischmetal is unstable in air, oxidizing very rapidly and progressively. Therefore up to 30% of iron is alloyed with it, forming an eutectic composition, and imparting to the alloy a desirable degree of moisture resistance and hardness. The rôle of hardness in both the sparking metal and the "striker" was also investigated by Hillstrom[133] who did not, however, attain a significant insight into the problem. The more pyrophoric the metal, the less kinetic energy on impact is required for sparking.

Earlier, it was mentioned that there is a sparking tendency in other alloys such as Zr-Sn and Zr-Pb. Other candidates, no doubt, exist. Very hot sparks are also obtained from uranium. Depleted uranium has been used as a pyrophoric spark generator for spotting rifle projectiles by adding 50% by weight to mixtures of potassium perchlorate, barium or ammonium nitrate, and magnalium. Kinetic energy penetrators were developed for the United States Air Force rapid-fire gun from uranium alloyed with 0.75% titanium[227]. Low concentrations of titanium impart significant corrosion protection to uranium so that cladding is not required. Ignition of uranium fragments has also been investigated and the interested reader is directed to Volume 10 of Fedoroff *et al.*[72] Intermetallic compounds of uranium with bismuth, tin, and lead are also pyrophoric as fragments.

Pyrophoricity is of special interest in chaff as it is used in decoys. Iron foil can be activated[13] much in the same manner as is Raney nickel (see Chapter 16), and many other elements can similarly be made to self-heat when exposed to air, thereby generating an infrared signature. Pyrophoricity is sought in incendiary munitions; the use of pyrophoric alloys, zirconium and titanium sponges, and depleted uranium has been recommended for the formation of long-duration hot sparks which would be of value in the ignition of aircraft fuel. The advent of low vapor pressure aviation fuels and of supersonic aircraft has presented special problems in the destruction of targets which have not yet been solved with pyrotechnic devices.

Depleted uranium is not used as a flame carrier, for reasons which may be political as much as anything else. The design characteristics, reaction modeling, target simulation, and thermodynamic parameters required for pyrophoric fragment generators are exhaustively reviewed in an old study by the Denver Research Institute[42].

Intuitively one would associate pyrophoricity with the ability to act as a flame carrier, but to date no quantitative studies of this matter have been performed.

A variant mechanism for the generation of pyrophoric fragments by impact is based on shock compression along the Hugoniot curve of the porous mixture[97]. Distended metals in the form of powders or sponge are considered to be of particular pyrophoric value because the shock wave causes work to be performed on compaction, generating a persistent hot zone which is sufficient to ignite the mixture (see Chapter 13).

Table 10-2 lists the elements in approximately decreasing order of pyrophoricity, although evidently the ranking could be changed by differences in hardness, compaction, and the presence of contaminants. Temperature and surface area are additional variables of importance. Pyrophoric elements, as shown in Table 10-2, are also characterized by largely unfilled *d* electron orbitals. Certain elements spark particularly well when alloyed as eutectics in which the composition is rich in the pyrophoric element. Pyrophoricity is lost when the alloying agent forms an intermetallic compound (*i.e.*, alloys exothermically). Compounds lose electrons from the conduction band and the loss of pyrophoricity may be related to this.

The sparks and the glitter seen in fireworks are caused by somewhat different phenomena. The *tremalon* or glitter effect is discussed in detail in Chapter 15.

A quite separate matter from pyrophoric ignition is the ignition of dust, which can be the cause of spectacular explosions. The flammability of dusts varies greatly with substance, particle size, and surface history of the dust. Common dust explosions in grain elevators, etc., are not directly an aspect of pyrotechnics, but a few remarks are not amiss because the phenomenon is very much an aspect of industrial safety also of concern to the pyrotechnics industry. There is a large body of specialized literature dealing with dust explosions. In some pyrotechnic operations, as in the Løvold process for making black powder, or in the mixing of flash powder, one must be conscious of the tendency of powdered mixtures to pick up large electrostatic charges, requiring the mixing equipment to be grounded. No path for electrostatic conduction into and out of the mixture should exist. The need for strict humidity control has been emphasized.

Dust explosions resemble gas explosions in the enormous force that both exert on structures. These explosions maintain their pressure for much longer periods than do those of high explosives (*i.e.*, for many milliseconds instead of microseconds). With respect to dust explosions, this is true because the density of a dust/air mixture is much lower than that of a solid explosive. Whereas dust explosions are somewhat remote from the subject covered in this book, the hazards associated with the handling of metal powders are one source of danger associated with handling and preparation of pyrotechnic devices. Static electrical discharges, such as those caused by the handling of certain plastic films and bags, coupled with the discharge from ungrounded conductors or from ungrounded personnel, are known to have been the cause of many accidents. Use of such paraphernalia as antistatic compounds, grounding straps, conducting table-tops, and conductive wrappings is familiar to the explosives industry and these should be considered worthwhile safety precautions when formulating pyrotechnic compositions as well.

Accidents involving flammable dusts frequently occur in two stages – an initial "blow" which disperses more material that may in turn ignite, either from the original flame or a static discharge. The danger may persist for some time, considering that particles of 100 microns in size settle at about 0.5 cm/sec. Because of nondirectional turbulent flow of air in a room, fine particles (including metal powders) are readily dispersed during handling.

It is difficult to rate combustible powders in terms of their hazard, because in addition to particle size, their surface condition plays an important rôle. Anyone familiar with the handling of zirconium will know the passivating effect of storage in a humid atmosphere. Likewise, in the manufacture of black powder, the maintenance of an absolute humidity of 20,000 ppm of H_2O in the air is a minimum safety measure. The relative humidity in a cold climate offers insufficient protection against static accumulation. So does the abnormally low humidity of arid regions, where many manufacturers of – and testing facilities for – pyrotechnic items are located, usually with the safety advantage of isolated location.

Fuel-air explosions are an example of an ordnance technique, and like dust explosions are not truly pyrotechnic. A relatively large quantity of a hydrocarbon is explosively dispersed over a target, *e.g.*, enemy troop concentrations, then to be initiated by a properly timed second event, thereby achieving both a hot flame front and a significant overpressure. It seems a good idea in theory, but has not been made to work reliably.[143]

Hypergolicity: Self-igniting Fuel-Oxidizer Systems

Many spontaneous or easily induced incandescent reactions occur with a fuel and oxidizers other than air. For example:

- Halogens and halogen compounds with fuels
- Water activated systems
- Liquid oxidizers and fuels
- Spontaneous reactivity of solid oxidizers with solid fuels

Elemental halogens form a series with decreasing reactivity. In principle, the reactivity of fluorine is quite impressive, but its high vapor pressure and high reactivity have reduced it to a laboratory curiosity. Its compounds with oxygen, nitrogen, and chlorine have found application as oxidizers in rocket engines. The only convenient solid source of fluorine is cobalt pentafluoride, but it is too reactive to be considered in a pyrotechnic mixture. A mixture of Teflon, a polyfluorinated polyethylene, with magnesium, is a popular deflagrating agent, but not an example of a self-igniting system.

Chlorine, in chlorinated hydrocarbons, is said to be explosive when in contact with alkali metals[70]. Even triethylaluminum has been reported to explode when mixed with carbon tetrachloride[70]. Solid organic chlorides, such as hexachloroethane in the presence of zinc, are of interest in pyrotechnic smokes (see Chapter 20).

In ordnance design in general, highly reactive components of fuel-oxidizer systems are a poor choice as long as a similar effect can be achieved with less active substances. One must consider not only the difficulties of handling such materials prior to loading, but also the consequences of leakage during storage of the finished item.

Water may cause spontaneous ignition in some fuel-oxidizer systems without taking part in any chemical reaction at all. At standard temperature and pressure, aluminum powder mixed with iodine will not react until wetted with water. Magnesium powder when mixed with silver nitrate also bursts into flame upon moistening. The water appears to act as an electrolytic conductor. An Italian patent[70] refers to a water-actuated incendiary mixture consisting of powdered magnesium, anhydrous copper sulfate, ammonium nitrate, and potassium chlorate. The water permits the reduction of the copper by magnesium and the anion exchange reaction results in the formation of unstable ammonium chlorate. This patent claim is a good illustration of the danger of mixing chlorates with ammonium salts, particularly in the presence of a reducing agent.

Self-ignition under the influence of moisture has another and more complex effect which has often plagued fireworks manufacturers. In fireworks formulæ with chlorate and sulfur, the oxidation of the sulfur in the presence of moisture can lead to acidification of the mixture. In the absence of neutralizers, chlorine dioxide or chlorine and oxygen are evolved, which, in turn, act as strong oxidizing agents. If the rate of the moisture diffusion is slow, nothing worse than the decay of the composition will result, but spontaneous ignition has been known to happen.

Under ordinary conditions, alkali chlorates in combination with fuels do not ignite spontaneously. The chlorates of the alkaline earths and of heavy metals are less stable, and spontaneous ignition can occur quite readily with a number of fuels and in the presence of moisture.

Potassium chlorate has caused deterioration when used commercially in such items as railroad fusees, due to double decomposition reactions with other salts. These examples show the relative instability of chlorate-containing systems when exposed to moisture. However, in matches where chlorate, sulfur, and organic binders are combined and exposed to the atmosphere, decomposition is virtually unknown. This shows that proper formulation with inclusion of acid-neutralizing substances can successfully break the chain of undesirable oxidation-reduction reactions.

Fuming nitric acid has the ability to oxidize many organic compounds vigorously in an incandescent reaction. The reactions not only furnish heat and fire, but produce only gaseous reaction products and are therefore used in self-starting, "hypergolic" rocket propellant combinations. Inhibited red fuming nitric acid (IRFNA) in combination with unsymmetrical dimethyl hydrazine (UDMH) is one example of a hypergolic couple. Several acid derivatives have very strong oxidizing power and some of them have been tried as igniters for hydrocarbons in flame throwers. Examples of extremely reactive low-boiling substances are chromyl fluoride, CrO_2F_2, chromyl nitrate, $CrO_2(NO_3)_2$, perchloryl fluoride, ClO_3F, as well as nitrosyl perchlorate.

In contrast to these substances, which are not usually practical for pyrotechnic purposes, there are combinations which are noncorrosive and quite harmless in storage. For instance, a mixture of potassium chlorate and sugar can be initiated with a drop of concentrated sulfuric acid.

The oxidative power of permanganates surpasses that of chlorates in some respects. Glycerine brought together with dry crystals of potassium permanganate bursts into flame a few seconds or minutes after contact. On the other hand, a more reactive and less viscous organic fluid such as dimethyl sulfoxide (DMSO) flashes instantaneously when dropped onto finely powdered potassium permanganate. This is a hitherto unadvertised use of DMSO. Potassium permanganate is, due to its unusual reactivity, an interesting material, although unsuitable for industrial pyrotechnic applications.

One combination of two solids exists in which a flaming or even explosive reaction may take place by merely pushing the powders toward each other or upon exertion of very slight pressure. The two materials are red phosphorus and potassium chlorate. A demonstration of their reactivity should be performed only with a few milligrams of each component. Disasters have been recorded when high school students have appropriated and mixed these two chemicals together; controlling their availability at the same time to inexperienced persons is an essential safety precaution.

Nevertheless, this reaction is one of the most interesting and most useful solid reactions, having been tamed in the modern safety match, which is discussed in the next chapter. Red phosphorus and potassium chlorate can be mixed in comparative safety when both reactants are thoroughly moistened before they come into contact. Small amounts of such a mixture, combined with an aqueous binder solution, form the explosive composition of toy caps. If alcohol or ether is used as the vehicle, it is possible to load larger amounts of the mixture into specially designed containers that allow the liquid to evaporate. A variation of this item has been proposed as an anti-infiltration device, causing flash and sound, but no injury. Larger charges would make formidable antipersonnel mines because a slight pressure will explode the devices.

Chapter 11

Matches

The common match must surely be one of the great conveniences of our civilization. Its development spans several centuries, and at each stage the solution of the technical problems presents interesting lessons. Passing over the long history of fire sticks, punk, and flint and steel, the story proper begins in 1674 with the discovery of white phosphorus by Brand who distilled the dried residue of urine with charcoal in a retort. The Honble. Robert Boyle used the condensate from this process (white phosphorus) to ignite sulfur-tipped wood splints.

Between 1780 and 1830, numerous contrivances approaching the individual match concept were introduced, but not without acrimonious claims and counterclaims regarding their priority. Pyrotechnic friction matches, from about 1835, were called "Congreves" in Britain, after the inventor of the famed military rocket. These contained as much as 20% white phosphorus. By reducing the phosphorus content to about 5%, and by adjusting the other ingredients such as sulfur, rosin, potassium chlorate, and binders, the quality of these matches was greatly improved. No basic change in formulation had taken place by the time the phosphorus match declined in use toward the end of the 19th century, except that the sulfur in the splint with its pungent burning odor was replaced first by beeswax and finally by paraffin wax.

The poisonous qualities of white phosphorus became apparent only rarely in ordinary customer use, when the tips of matches were chewed by children. However, workers exposed during the manufacture of the matches to the fumes of white phosphorus (which entered the body mainly through defective teeth) were subjected to an incurable destruction of the jaw bones, the so-called phosphorus necrosis or "phossy jaw." This condition was perhaps the first occupational illness to be diagnosed as such. With the growth of awareness of its social costs, all civilized countries either prohibited the use of white phosphorus in matches or taxed the matches out of existence.

While it was possible to make a match that ignited by friction on any surface without the use of white phosphorus, none could equal the ease of handling of the phosphorus match. The problem was finally solved satisfactorily by an invention made by two French chemists, Henri Sévène and Emile David Cahen. The United States patent was acquired by the Diamond Match Company in 1900 and offered to other companies for the production of safe, nonpoisonous "strike anywhere" (SAW) matches. The significant ingredient was the nontoxic tetraphosphorus trisulfide (P_4S_3), customarily called "sesquisulfide" in the trade, and made by fusing P and S in the absence of O_2. There are both single tip heads (in Europe) and double-tipped heads (in the United States) which are described below.

The most important type of match is the one utilizing potassium chlorate (discovered by Berthollet,* *ca.* 1786, who prepared the chlorate by the action of chlorine on potassium hydroxide). What might be called the first two-component pyrochemical fire-making device was based on the property of chlorates to produce flame in the presence of a fuel when moistened with strong sulfuric acid. Chancel's instantaneous light box or *briquet oxygéné* (1805) consisted of a match tip of potassium chlorate, sulfur, binder, and other ingredients on a wooden splint. Pressed against asbestos saturated with concentrated sulfuric acid, carried in a glass vial, this device furnished a flame, often accompanied by sputtering and spraying of acid, which rendered its use unsafe. However, the invention in one form or another stayed popular for many years. A variant of this type, the invention of Samuel Jones (1828), is described below by Charles Darwin[70] recounting his visit to a Brazilian plantation in July 1832 during the early months of his famous circumnavigation of the world:

> I carried with me some "promethean" matches, which I ignited by biting; it was thought so wonderful that a man should strike fire with his teeth that it was usual to collect the whole family to see it: I was once offered a dollar for a single one.

The match described consisted, according to other sources of information, of a small glass ampoule containing diluted, blue-colored sulfuric acid and coated with a sugar/chlorate/binder mixture. The whole was wrapped compactly into an eight-centimeter long piece of paper. For the less courageous, breaking the vial with pliers was recommended and these were sometimes furnished with a kit. The lengthy and complex history of the match was recently described in detail by S. Johansson[123].

The true friction match – the immediate precursor to the safety match – was the invention of John Walker of England, *ca.* 1826. It contained potassium chlorate and antimony sulfide and could be ignited with some skill between the fold in a piece of abrasive "glass paper". More sensitive "lucifers" or "locofocoes"† followed, which contained sulfur in addition. The modern safety match came about only with the addition of red phosphorus. By leaving the chlorate in the matchhead and placing the phosphorus on the friction surface, Pasch in Sweden (1844) provided a concept which eliminated most of the hazards of the earlier matches. The United States was slow in accepting the safety match. The big kitchen match, which could be taken out of the pocket and struck with one hand on the shoe sole or any other hard surface, was more suited to the American temperament. The final chapter in the history of the safety match was the invention of the paper match, now called the book-match, by Joshua Pusey (1892). Somewhat more difficult to handle than the wood stick match, these inexpensive, advertisement-carrying matches gained only gradual acceptance, but they now dominate the American match industry.

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* Claude Louis Berthollet (1748-1822) must not be mistaken for another important French chemist, Marcellin Pierre Eugène Berthelot (1827-1907). Both were interested in gunpowder and explosives, which adds to the possibility of confusion.

† "Locofoco" acquired a political connotation at this period, being applied to the more extreme adherents of the Democratic party.

At or near the peak of American match production in 1958,[70] forty billion matches were produced annually, three-quarters of which were the cardboard variety. By the 1970s, inroads made by the disposable lighter were considerable; however, the match industry remains the largest producer of a pyrotechnic product. The economic value of fireworks and other civilian items, such as railway or highway signals, is only a small fraction of the amount spent on matches. Because of their highly mechanized, high-speed manufacturing methods, and the support of advertising, book matches are the cheapest and most popular form of flame producers in the country.

Manufacturing Procedures

Book matches are punched from 0.038-inch thick, lined chipboard in strips of one hundred splints, each having a 0.125-inch width. A single machine can produce twenty million match splints in one eight-hour shift. It requires only half an hour to convert raw chipboard into completed, strikable matches, ready for cutting and stapling into "books." In this half hour, the tips of the punched-out splints are first immersed in molten paraffin wax, in order to produce a persistent flame and make fire transfer possible. The tip composition is subsequently applied by dipping the ends of the strips into a thick but smooth fluid suspension carried on a cylinder rotating in a tank at the same speed as the match strips move. While an evenly rounded match tip is formed, cold air is blown against the matches, which then enter a dryer. There, however, the main object is not so much the speedy removal of the water in the match composition as it is the congealing of the matchhead, which takes place quickly at a relative humidity of 45-55%.

The matchbook cover is equipped with a striking strip, applied by a roller-coating process using a slurry of a composition described below. The cover may be previously printed with the advertising message.

Wooden matches can be made by the veneering method whereby aspen wood is peeled off a section of a log and cut into splints having a square cross section of 0.2 to 0.35 cm, depending on the length of the match. The alternate method consists of cutting rows of round splints from selected blocks of white pine by means of individual dies that resemble a large darning needle, of which the eye is the cutter.

A third type of commercial match popular in Latin countries is the *vesta* with a center of cotton threads, or a rolled and compressed thin and tough paper, surrounded by, and impregnated with, wax, each match being in effect a miniature candle of long burning time (about a minute).

Two processes precede the affixing of the matchheads on wood or paper splints. The first one is glow-proofing of the splint by impregnation with ammonium phosphate or a mixture of this salt with boric acid. In paper matches, the impregnation is conveniently done during the fabrication of the paper. This suppresses continuation of glowing of the carbonized splint after it is discarded, and prevents the burned part with its hot tip from falling off and singeing clothing. The second impregnation is the soaking of paraffin wax into the stem for a certain length to assure flame forming and fire transfer to the wood. Head formation is similar to the process described for book matches, except that for SAW matches, a second smaller tip is affixed to the larger bulb. The rollers in the dipping tank over which the splints travel are grooved for the SAW tip. The same equipment can be used for safety matches simply by leaving out the second dipping. Immersion of the tips in diluted formaldehyde solution "tans" gelatine-based binders (such as animal glue) and hence aids congealing and facilitates subsequent proper drying of the matchhead.

Non-Standard and Military Matches

Because match manufacturing is a series of high-speed, highly mechanized operations, any variation that involves dimensional or procedural changes is a major undertaking warranted only if a continuous, high-volume production is forthcoming. Thus, a customer may be accommodated, for a price, if he desires an unusual shade of color for the tip or striking strip. However, major variations in the formulæ and, especially, in the size of the heads, cannot be tolerated. Hence, specialties, which occasionally appear on the market, must be classed as toy fireworks or special production items, made laboriously and at relatively high cost by hand-dipping. Such matches produce a colored flame (Bengal matches), give off perfume or fumigating vapors, explode, or furnish a persistent glow or flame for the purpose of burning in strong draft. In order to do these things effectively, an enlarged elongated bulb is generally used.

Matches burning with a colored flame are popular in Germany as miniature fireworks. A high content of gas-forming fuels and especially a small amount of phosphorus sesquisulfide makes matches wind-resistant. If, on the other hand, no visible flame is desired, as might be the case in a military operation at night, a flameless match can be formulated to burn with a strong glow front along an elongated bulky matchhead. Addition of powdered charcoal with other proper adjustments will produce this effect. Such a match would be commercially unacceptable because of the fire hazard, but is excellent for igniting safety fuse.

An interesting variation of the regular match is the "pull-match". It is a paper match, considerably thinner and narrower than the regular book match, since it needs very little stiffness when being used. The tip part of the match is enclosed in a strip of corrugated paper glued to a flat cardboard (such as a box of cigarettes) and the inside of the corrugated board is covered with striking material. On pulling the match fast enough out of the corrugation, the tip passes and engages the striker and ignites.

A variation of the pull-match is the commercial pull-wire fuse lighter. A similar article has the military designation M1 Friction-Type Fuse Lighter; in this, the rôles of the striker and match are reversed. The match mixture is located in a metal cup, and a length of wire, corrugated and covered with striking mixture near the end, is threaded through a hole in the cup, with a loop for pulling the wire through it. The match cup is enclosed in a length of stiff paper tubing for the insertion of a delay fuse, held in fixed position in the tube by a metal ferrule with sharp protrusions. On removal of the wire with a sharp pull, this cheap device will fairly reliably produce a spit of flame to ignite the fuse train[9].

Years ago, the "repeatedly ignitable" match aroused interest because of exaggerated claims for its performance, based on the patents by Rezsö König and Zoltán Földi and numerous followers[70].

It was a small pencil-like rod, the central part of which was a safety-match composition, while the outer layer consisted of a slow and cool-burning mixture the effective ingredient of which was metaldehyde (sometimes combined with other volatile organic substances). These remain expensive chemicals to burn as flame-formers in lieu of paper, wood, or paraffin; in addition, they evaporate on storage. Repeated striking of a previously used match fouls the striking strip, and ignition becomes progressively more difficult.

The existence of a primary ignition device that can be blown out and reignited is a remarkable curiosity for the collector of odd pyrotechnical knowledge, but otherwise is scarcely competitive with normal match production.

Match buttons, ignited by hand with a striker such as the one on the wooden top of a railroad fusee, or on a separate strip under the lid, as in the M1 fire starter, are formulated simply according to MIL-STD-585 and the striker according to MIL-STD-537, though fusee manufacturers also use other proprietary formulæ. The aim of this system is to produce a hot and relatively slow and intense flame, affording transfer of fire to the substrate in which the match button is embedded. The compositions sometimes contain a non-hydrophilic binder such as shellac or nitrocellulose.

In order to understand the chemistry and formulation of the safety match, it should be emphasized that the reaction between potassium chlorate and red phosphorus, which is the basis of its function, is extremely hazardous and unpredictable. Their separation in match tip and striking strip is, therefore, not only a brilliant piece of inventive creation, but requires great ingenuity to strike a balance between effective action and safe action. The next point to consider is that the primary ignition must be controlled and followed by orderly progression of a flame, and that any kind of flashing or dropping of glowing particles must be avoided. This latter task falls to the various siliceous ingredients in the matchhead, which form a sintered residue containing all the nonvolatile residues from the reaction. Similarly, the phosphorus in the striker must be prevented from burning off or causing a shower of sparks. Choosing the proper grade of binder and its correct ratio to the phosphorus accomplishes this. Since ease of ignition, spark forming, and excessive wear of the striking strip all go together – while a more adhesive or stronger grade of binder decreases wear and tear, desensitizing

Table 11-1. Compositions for Commercial Matches

	1	2*	3†	3§
Animal (hide) glue	9-11	11	11	12
Starch	2-3	–	4	5
Sulfur	3-5	5	–	6
Potassium chlorate	45-55	51	32	37
Neutralizer (ZnO, $CaCO_3$)	3	7	6	1
Diatomaceous earth	5-6	–	–	3
Powdered glass, silica	15-32	15	33	21.5
Burning rate catalysts ($K_2Cr_2O_7$ or PbS_2O_3)	to suit	1	–	.5
Water-soluble dye	to suit	–	–	–
Black iron oxide (Fe_3O_4)	–	6	–	–
Manganese dioxide	–	4	–	–
Paraffin	–	–	–	2
Phosphorus sesquisulfide	–	–	10	3
Rosin	–	–	4	6
Dammar gum	–	–	–	3

* Given by Shidlovskii[214] as an European safety match composition.

† Tip composition for SAW match composition.

§ Base composition for SAW match, laden with combustibles for strong billowing flame but of low friction sensitivity.

the act of ignition – head and striker formulas must not only be precise in themselves but matched in behavior. The addition of finely powdered glass contributes to the resistance toward "striking through" and burning off the striking strip.

A similar but far more complex rôle is played by the binder in the matchhead. The glue must be strong enough to permit easy abrasion, which precedes ignition. The amount of glue to be used is constrained by its pyrochemical function as fuel; while the match is overladen with fuel with respect to oxidizer, a further excess of fuel beyond a certain limit would prevent the tip from flaming altogether, and the smoldering bulb would not reach the flame point of the wax in the stem. The match tip would simply fizzle out.

In modern high-speed match production, the type of binder in the matchhead is limited to one kind and to few grades of it. High-grade animal-hide glue, with the capability of quickly forming a reversible gel on cooling below 30° C from its more concentrated solutions, causes the other components to remain fixed in place once the dipping process is complete. Should the binder instead have a chance to form a "skin" in the top layer of the bulb, as happens with high molecular weight organic colloids in aqueous solution, the resulting "case-hardening" will convert the matchhead into a miniature bomb – the chlorate/sulfur/binder mixture will burn explosively under the slightest confinement. Before temperature and humidity control of match drying equipment came into general use, the unintentional explosion of a match was no rarity. This was not necessarily the result of faulty formulation, but mostly attributable to hot and humid conditions during manufacture, when the congealing of the matchhead at the start of the drying process was delayed or never took place.

To continue with the specific functions of the chemical ingredients in matches, we consider next the two functions of the sulfur in the head formula: it acts as an easily ignitable and hence somewhat sensitizing fuel and flame-former, and its combustion product is the pungent, but harmless and not nauseating, sulfur dioxide which masks the much more unpleasant odor of burning glue. Thus it is a "perfume" of sorts; its place can also be taken by powdered rosin. Table 11-1 illustrates a variety of compositions representative of those in current use.

Both matchhead and striker formulæ contain an insoluble but acid-neutralizing salt such as calcium carbonate (whiting, ground limestone). This functions to abort any tendency toward destructive oxidation of sulfur in the head or of red phosphorus in the striker. The latter process can be greatly accelerated by the catalytic influence of certain heavy metals, especially copper. In the past, this phenomenon has led to baffling destruction of the striking strip when copper bronze powder was used in the decorative artwork on the covers of matchbooks.

Apart from the noted exceptions, it can be said that both matchhead and striker are of practically limitless stability even under highly diverse conditions of storage. Dr. Ellern reports that he kept book matches without special protection under midwestern climatic conditions for more than 40 years. These remained in perfect condition except for some deterioration of the cardboard.

The least understood component of the matchhead formula is potassium dichromate – once generously present in many formulæ[69, 70, 78, 214]. It controls the burning rate and facilitates ignition following the "prime" reaction between chlorate and phosphorus: even minute percentages exert a noticeable influence. It can be replaced by lead compounds (such as lead thiosulfate) and, in general, by compounds that furnish finely-divided oxides of metals that can occur in several valence states. This parallels the influence of similar compounds in lowering the decomposition temperature of molten chlorates, and these additives can be referred to as "catalysts" even though their precise functioning is obscure.

Table 11-2 lists striker or "friction" formulæ for commercial safety matches. Nowadays, the binder is always rendered insoluble after application either by a special hardening process[70], formaldehyde treatment, or the use of a casein solution in ammonia. This prevents the staining formerly experienced when matchbooks were carried in shirt pockets and subjected to perspiration or exposed to rain. The striking strip can also be made with hydrophobic binders such as nitrocellulose or various plastic emulsions, but the quality of these moisture-resistant strikers is generally inferior, as are all special formulas designed to make the striking strip adhere to foil, plastic, metal, or other impervious surfaces.

The color of the striker may be varied by omitting carbon black or charcoal, and tinting or lightening it with various pigments such as water-dispersable

Table 11-2. Safety Match Striker Compositions

	1	2*	3†
Animal glue	–	16	9.3
Dextrin	20	–	7.0
Red phosphorus	50	50	37.2
Antimony sulfide	–	–	33.5
Iron oxide (Fe_2O_3)	–	–	7.0
Manganese dioxide	–	–	3.4
Calcium carbonate	–	5	2.0
Powdered glass	30	25	0.6
Carbon black	–	4	–

* Shidlovskii[214].

† Casein and animal glue plus hardener of U.S. Patent 2,722,484.

titanium dioxide, hydrated iron oxide, etc. Even bolder colors are possible but not practical.

The typical European match, because of its use of dark oxide pigments, leaves no chance for æsthetic variety, but there are brightly colored matches outside the United States; matches from the far East now often appear in delicate pastel colors or white.

Antimony sulfide in match or striker formulas is shunned in the United States. It is (or was) a strategic and critical material, as well as being fairly expensive and tending to settle out because of its high specific gravity. It can partly replace red phosphorus because of its low ignition temperature and its reactivity with chlorates.

Table 11-1 contains two typical compositions for SAW matches, but each fulfills a completely different function: the tip, which is easily ignited by rubbing over any solid surface, and also by scratching, stabbing, and (less reliably) breaking up (crushing), contains a rather large amount of phosphorous sesquisulfide. This is the easily ignitable agent on the tip. The bulb or base is laden with fuels that provide a billowing flame, and (with the addition of some sesquisulfide) becomes the major contributor to the moderate wind resistance of this type of match. If blown out immediately after ignition, a well made SAW match should "come back" with full flame once or twice. The chlorate content of the base is deliberately kept low in order to desensitize the bulb: since the large SAW matches are packed several hundred to a box with half of the heads at each end, touching each other, a large heavy impulse can cause a sizeable amount of friction which might be sufficient to ignite a high chlorate formula of this type.

Properties of Matches: Mechanism of Performance

The act of striking a safety match consists of bringing matchhead and striking strip into intimate contact by rubbing so that reaction between chlorate and phosphorus can occur. It is open to argument whether mechanical action creates a minute "hot spot" from which the reaction spreads, or ignition takes place through intimate contact of chlorate and phosphorus. When one rubs a match very lightly over the striker in complete darkness, greenish sparks of burning phosphorus can be observed. Such mechanical force would appear to be stronger than necessary to break through the surrounding glue layers. Normal, stronger rubbing permits the tiny flash from the chlorate/phosphorus reaction to ignite the glue/sulfur/chlorate system, aided by the catalytic influences of the heavy-metal additives, *viz.*, dichromate, lead thiosulfate (in some American matches), and manganese dioxide and others in European matches.

Safety Aspects

Safety matches can be set off by impact or strong friction. This in no way detracts from the safety aspect since it takes great skill to ignite a safety match in the absence of a phosphorus striker. Such ignition can be achieved by rubbing the match over a glass plate or a piece of fairly smooth and dense cardboard with just the proper pressure to create enough heat to ignite the match mixture by friction but without breaking up the fragile match tip. A blow with a hammer will explode a safety match, and sulfuric acid will ignite it like other fuel/chlorate mixtures as discussed in the preceding chapter.

On the other hand, considering that the safety match tip mixture has both explosive and primary ignition characteristics, matches in normal confinement (as in a matchbook) are extremely safe. Experiments have been performed in which matches in regular cardboard shipping cases were ignited by setting off electrically a single match book in the standard carton of 50 books, 50 cartons to the case. In every instance, the flash from the ignited book spread only to the other books in the same small carton and often only to a few of these books! There is not enough oxygen present to propagate their initial fire, nor does the heat from all the matchheads amount to much in relation to the large mass of the paper. It is, however, different when cut-off matchheads are accumulated and set off in tight confinement, as many deplorable accidents involving young rocketeers have shown.

The question of heat output and flame temperature of a single matchhead is sometimes raised. A single matchhead, without involvement of paraffin and paper, should furnish about 14 calories. This heat is only one-tenth or less the heat of the burning paraffin, not including the paper. The flame temperature ranges from 1350° to 1930° C[70].

Claims concerning matches "going off" or "blowing up" spontaneously can generally be attributed to violent striking, ignition of a cracked bulb, or careless handling of the lit match leading to ignition of the whole book. Also, if more than one single book is carried in one pocket, interlocking may increase the risk of accidental ignition.

Generally, matches, when heated in an oven, ignite spontaneously at 180°-200° C. Strike-anywhere matches ignite under the same conditions at about 120° C: higher than the self-ignition temperature of phosphorus sesquisulfide at about 100° C.

Toxicity

Small children are inveterate explorers of all objects within their reach and, apparently, the slightly bitter and salty taste of matchheads is no deterrent to chewing and sucking. The toxicity of matches thus becomes a frequent subject of concern to parents and medical practitioners. While potassium chlorate may cause disturbances if ingested in large quantities, the amount contained in one match is very small (about 9 mg) and the amount a small child can suck out of one – or even a few books – should be below a toxic limit. Osol and Farrar, as reported by Ellern[70], give 1 g as the maximum therapeutic (*i.e.*, nontoxic) dose of potassium chlorate for an adult. The other ingredients are either harmless or present in such minute quantities that they can be regarded as such. Therefore, while safety matches cannot be recommended as part of a steady diet for infants, anxious parents need not be unduly disturbed if they find their child chewing up a book.

Since most laymen do not realize that two major kinds (allotropes) of phosphorus exist, the word "phosphorus" may evoke the spectre of phosphorus poisoning where there is actually no need for concern. It is generally agreed that red phosphorus is nonpoisonous, though with the qualification "when pure." People have handled red phosphorus daily for decades in preparing striking mixtures without any ill effects, even though no special precautions as to contact with it were taken.

Humidity Resistance

During World War II the requirement arose for matches which would be ignitable after submersion in water for six hours. This desideratum was fulfilled by partially coating kitchen matches with a nitrocellulose lacquer of proper thickness and flow characteristics so that the coating was reasonably uniform and did not accumulate near the tip, which could make the striking difficult or explosive. Dr. Ellern had no difficulty in producing his formula WM-49, which was an underplasticized NC solution with added cellulose acetate-butyrate to arrest back-flow (because of its gelling properties). Millions of matches characterized by a deep green color in the lacquer were then manufactured. They could withstand water immersion at ambient temperatures for as long as ten hours.

Actually, matchtips cannot be made highly humidity-resistant in themselves because of the eventual breakdown of the water-soluble chlorate, the softening of the glue under prolonged extreme humidity, and the relatively small amount of binder in a matchhead formula. Safety matches can be made to withstand a limited exposure to extreme conditions. The military test (FE-M-101H, Oct. 31, 1964) consists in exposing the matchbooks in a strictly specified manner over water at 40° C for 8 hours. It is not practical to coat safety matches with a lacquer because of difficulty in striking, which increases with the effectiveness of the coating. A heat-sealed envelope will protect a book or box of matches from moisture. During prolonged storage this is simple and effective, though somewhat costly.

Because the SAW tip is vulnerable to prolonged exposure owing to the sesquisulfide content, the conclusion seems inevitable that where a certain water-vapor transmission exists, no matter how small, and where the exposure fluctuates, the "better" protection is one with a thinner lacquer layer which will promote more rapid equilibration with the environment. This is no more than a general recommendation. Only an analysis of the effects of moisture, time, periodicity, and temperature extremes on performance can aid in deciding the best method of protection.

Chapter 12

Primers and Ignition Mixtures

The use of primers as a means of initiating a pyrotechnic event came about only during the nineteenth century. Before that, initiation was by open flame, spark (as in a wheel- or flintlock), or a fuse train. Black powder was the universal flame carrier, propellant, explosive and hence, the mainstay of pyrotechnics. A primer will generate fire when struck mechanically, heated, shocked, or stimulated electrically. Impact-sensitive materials became known quite early, primarily the fulminating compounds of silver and gold. Mercury fulminate was apparently known to Johann Kunckel von Löwenstern (1630-1703), but was forgotten and re-discovered by Edward Howard at the beginning of the nineteenth century[44]. It was widely used as a primary explosive until gradually supplanted by lead styphnate and lead azide in the mid-twentieth century[72]. Compounds of this class are called primary explosives, and their use represents a technology in which explosives and pyrotechnics overlap. The interested reader may wish to pursue the subject further[74] than is feasible in this book.

Among the first modern primers were those of the Rev'd. Alexander Forsyth, the sporting parson of Belhelvie, Scotland. His patent of 1807 mentioned both mixtures based on mercury fulminate and those based on potassium chlorate in combination with sulfur, charcoal, and other fuels.

The terms "primer" and "detonator" are by no means interchangeable, in that a primer serves to initiate a burning or deflagrating process whereas a detonator generates a shock sufficient to initiate a high explosive. Primers which initiate from a mechanical action are classified as percussion primers, stab primers, and friction primers. In pyrotechnics, the output of a primer serves to ignite an ignition mixture.

Percussion Primers

A percussion primer typically consists of a primer cup which contains the primer composition, an anvil against which the crushing or grinding action takes place, and sometimes a sealing closure. Although the cup is indented on firing, it is not perforated and so continues to function as a gas seal. The confinement of the gases not only increases the efficiency of fire transfer but aids in reproducing the desired delay time of sealed pyrotechnic devices which must function independently of ambient conditions.

A percussion primer produces a deflagration with hot particles, flame, and gases. The performance is measured in terms of closed bomb data from which pressure, rise-time, and volume of gaseous products are obtained[206]. With the appropriate equipment, variations in primer output within production lots and production runs can be measured. Present priming compositions can best be divided into corrosive and non-corrosive formulations. The corrosive type invariably contains potassium chlorate, whereas the non-corrosive types contain lead styphnate, as shown in Table 12-1. Corrosive primers are so called because potassium chloride, produced by decomposition of the chlorate, is deposited in the bores of weapons fired with ammunition so primed. Unless carefully removed, this residue corrodes steel rapidly and severely. Non-corrosive primers are free from this disadvantage as respects smalls arms. For detonators and percussion primers in one-shot applications (*e.g.*, a flare cartridge), the corrosive type poses no real problem and may, in fact, be preferable for reasons specific to the application.

When the United States became involved in the space program, a need arose for initiators capable of withstanding long-term exposure to high temperatures. Composition G11, shown in Table 12-1, was developed in response to the need for primers which might see temperatures in excess of 200° C.

Additional percussion primer compositions of both corrosive and non-corrosive types are shown in Table 12-2.

Stab Primers

Stab primers incorporate the more brisant lead azide. They may be used to initiate a detonation. Lead azide is hydrolytically unstable, causing it to deteriorate on storage, a process which is accelerated by vapors from plasticizers. The resulting hydrazoic acid attacks copper and copper alloys, producing copper azide. Copper azide, like many metallic azides[74], is unstable and may cause accidental initiation. The search for stable, stab-sensitive, flash-sensitive, and hot-wire sensitive substitutes (other than lead styphnate)[83] has produced notable success, resulting in the use of CP*, KDNBF† and DXN-1§ (previously called DXW-1). Appendix IV provides some additional details.

Additional formulæ for stab primer mixtures are shown in Table 12-3. Stab primer mixtures are not stoichiometrically balanced, but are oxygen-deficient. The autoignition temperatures range from 270° to 340° C. Stab primer mixtures are the densest of all primer compositions, with densities ranging from 1.3 to 2.0 g/cm^3. High density tends to reduce the ignition energy required, because the firing pin will deposit the energy over a smaller travel distance. The stability of stab mixtures is poor because the mixtures are hygroscopic, requiring careful sealing of devices.

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* CP = 2-(5-cyanotetrazolato) pentaammino-cobalt (III) perchlorate

† KDNBF = Potassium dinitrobenzotrifuroxan

§ DXN-1 = Mercury (II) *bis*-5-nitrotetrazole[137]

Table 12-1. Typical Priming Compositions[138]

Component	Non-Corrosive	Corrosive	
	PA 101	FA 70 Low Temperature	G11 High Temperature
Lead thiocyanate	–	25	–
Potassium chlorate	–	53	53
Antimony sulfide	10	17	25
Trinitrotoluene (TNT)	–	5	–
Calcium silicide	–	–	12
Basic lead styphnate	53	–	–
Barium nitrate	22	–	–
Aluminum	10	–	–
Tetracene	5	–	–
TACOT*	–	–	10

* TACOT = Tetranitrodibenzo-1-, 3a-, 4-, 6a-tetrapentolene[72]

Stab primer mixtures are particularly sensitive to static electricity, with spark initiation energies ranging from 0.0002 to 0.005 J. The Bureau of Mines has established 0.01 J as being normally safe for explosives handling by personnel. Impact initiation energies range from 0.08-0.1 J (determined by a 56 g weight). Such data are to be accepted with caution as they depend on the apparatus used for their determination, as well as on the quantity, prior history of compaction, humidity, and sample configuration.

Electrical Primers

Typical formulations for electrical primer mixtures are shown in Table 12-4. The stability and sensitivity data are generally higher than those of stab primers. They are loaded less densely than the other mixtures. The ingredients for these differ somewhat from the ones described earlier, showing the great variation of materials suitable for ignition mixtures.

The selection of ignition mixtures depends on the application. One distinguishes between "first fires," "starter mixtures," and "fuel mixtures." Ignition may be effected by a primer (see above), a hot bridgewire, an exploding bridgewire, a laser, or by shock (see Chapter 13). Table 12-5 lists typical first fire formulations.

Examples of fuel mixtures are given in Table 12-6. These generate gas on reaction, and therefore are used as heat sources for dissemination of chemical agents or smoke (see Chapter 20).

Table 12-7 lists typical ignition mixture formulations. They resemble first fire mixtures in many ways, but owing to their higher electrical and thermal conductivity, they are (as a rule) not as sensitive to electrical initiation or initiation from a primer. These formulations are given only for illustration and must be tested

Table 12-2. Percussion Primer Compositions[160]

	1	2	3	4	5	6	7	8	9
Potassium chlorate	50	–	37	53	–	–	35	–	–
Antimony sulfide	20	10	–	17	–	10.3	30	7	15
Lead dioxide	25	–	–	–	–	10.3	–	9	–
Trinitrotoluene (TNT)	5	–	6	5	–	–	3	–	–
Basic lead styphnate	–	60	–	–	–	–	–	–	–
Tetracene	–	5	–	–	5	3.1	–	12	4
Barium nitrate	–	25	9	–	–	31.0	–	22	32
Aluminum	–	–	–	–	–	–	–	–	7
Lead thiocyanate	–	–	38	25	–	–	17	–	–
Ground glass	–	–	10	–	–	–	–	–	–
Lead oxide (monoxide)	–	–	–	–	85	–	–	–	–
Boron	–	–	–	–	10	–	–	–	–
Normal lead styphnate	–	–	–	–	–	35.0	–	36	37
Zirconium	–	–	–	–	–	10.3	–	9	–
Calcium silicide	–	–	–	–	–	–	15	–	–
Pentaerythritol tetranitrate (PETN)	–	–	–	–	–	–	–	5	5

Table 12-3. Typical Stab Primer Compositions[160]

	1	2	3	4	5
Antimony sulfide	22	17	33	15	5
Potassium chlorate	45	53	33	–	–
Lead thiocyanate	33	25	–	–	–
Lead azide	–	5	29	20	–
Carborundum	–	–	5	–	–
Barium nitrate	–	–	–	20	39
Basic lead styphnate	–	–	–	40	–
Tetracene	–	–	–	5	2
Normal lead styphnate	–	–	–	–	38
Lead dioxide	–	–	–	–	5
Calcium silicide	–	–	–	–	11

Table 12-4. Typical Electrical Primer Compositions[160]

	1	2	3	4	5	6
Potassium chlorate	8.5	55	25	60	–	–
Lead mononitroresorcinate	76.5	–	–	–	–	–
Nitrocellulose	15.0	–	–	–	–	–
Lead thiocyanate	–	45	–	–	–	–
Diazodinitrophenol	–	–	75	20	–	–
Charcoal	–	–	–	15	–	–
Nitrostarch	–	–	–	5	–	–
Potassium perchlorate	–	–	–	–	66.7	66.7
Titanium	–	–	–	–	33.3	–
Aluminum	–	–	–	–	–	33.3

Table 12-5. Typical First Fire Compositions[160]

	1	2	3	4	5	6
Red lead, Pb_3O_4	25	50	25	–	55	70
Titanium	25	25	25	–	12	30
Black iron oxide, Fe_3O_4	25	–	–	–	–	–
Silicon	25	25	25	20	33	–
Barium nitrate	–	–	–	50	–	–
Zirconium hydride	–	–	–	15	–	–
Tetranitrocarbazole	–	–	–	10	–	–
Laminac	–	–	–	5	–	–
Red iron oxide, Fe_2O_3	–	–	25	–	–	–
Binder (Additional %)	–	–	–	–	8-10	–
Autoignition temperature, °C	762°	780°	865°	476°	777°	659°
Heat of reaction, cal/g	360	225	343	–	290	–
Burning rate, cm/s	0.88	0.88	0.64	0.25	0.64	0.40

Table 12-6. Typical Fuel Mixture Compositions[160]

	1	2	3
Potassium chlorate	42	–	–
Sugar	28	–	–
Magnesium carbonate	30	–	–
Nitrocellulose/acetone*	44	–	–
Ammonium nitrate	–	74	85
Charcoal	–	16	–
Potassium nitrate	–	8	–
Fuel oil	–	2	–
Rubber	–	–	12
Carbon black	–	–	2
Ammonium dichromate	–	–	1
Autoignition temperature, °C	176°	206°	214°
Heat of reaction, cal/g	365	406	602
Burning rate, cm/s	1.26	0.85	0.72

* additional percentage, used as a binder; 8% nitrocellulose in 92% acetone.

Table 12-7. Typical Ignition Compositions[160]

	1	2	3	4	5
Sodium nitrate	47	–	–	–	–
Sugar	47	–	–	–	–
Charcoal	6	–	–	–	–
Iron oxide, Fe_2O_3	–	50	–	25	–
Titanium	–	32.5	–	–	–
Zirconium	–	17.5	–	65	–
Nitrocellulose/acetone*	–	44	–	–	–
Boron	–	–	25	–	–
Lead dioxide	–	–	–	–	33.3
Potassium nitrate	–	–	75	–	–
Cupric oxide	–	–	–	–	33.3
VAAR†	–	–	1	–	–
Diatomaceous earth	–	–	–	10	–
Silicon	–	–	–	–	33.3
Autoignition temperature, °C	280°	456°	419°	427°	401°
Heat of reaction, cal/g	940	630	1524	–	–
Burning rate, cm/s	–	1.26	1.10	6.25	–

* additional percentage, used as a binder; 8% nitrocellulose in 92% acetone.
†additional percentage, used as a binder; vinyl alcohol-acetate resin.

Table 12-8. Typical Starter Mixture Compositions[160]

	1	2	3	4	5	6	7	8
Potassium perchlorate	30	–	–	–	–	–	–	–
Calcium silicide	35	–	–	–	–	–	–	–
Antimony sulfide	35	–	–	–	–	–	–	–
Nitrocellulose/acetone*	66	–	–	3	–	40	50	16.7
Silicon	–	26	–	40	–	–	–	26
Potassium nitrate	–	35	70.5	54	–	–	70.5	35
Charcoal	–	4	29.5	6	–	–	29.5	4
Iron oxide, Fe_3O_4	–	22	–	–	–	–	–	22
Aluminum	–	13	–	–	–	–	–	13
Potassium chlorate	–	–	–	–	43.2	43.2	–	–
Sulfur	–	–	–	–	16.8	16.8	–	–
Sodium bicarbonate	–	–	–	–	30	30	–	–
Corn starch	–	–	–	–	10	10	–	–
Autoignition, temperature, °C	446°	421°	418°	501°	216°	216°	401°	401°
Heat of reaction, cal/g	1812	1186	980	980	942	946	965	1102

* additional percentage, used as a binder; 8% nitrocellulose in 92% acetone.

Table 12-9. Ignition Requirements and Reaction Rates for Typical Ignition Mixtures

Mixture	Pressure, atm			
	0.1	20	30	Propagation Rate, cm/s
B/$BaCrO_4$	1.0 cal/cm^2		18.0 cal/cm^2	$1.29p^{0.073}$
B/KNO_3	1.5 cal/cm^2		2.5 cal/cm^2	$1.01p^{0.3126}$
B/$PbCrO_4$	1.0 cal/cm^2	10 cal/cm^2		$3.55p^{0.084}$
Al/$KClO_4$	35.0 cal/cm^2	5 cal/cm^2		$0.08p^{0.949}$

further prior to any application.

Starter mixtures (Table 12-8) often have the same composition as do other ignition mixtures except that in one case they may be blended dry and in another wet with nitrocellulose/acetone binder. They are often designed to be placed on the surface of other pyrotechnic or propellant formulations. Electrostatic sensitivity is high owing to the small fraction of electrically conductive constituents. Zirconium (as a fine powder) is very sensitive to static *despite* being conductive.

Ignition behavior of igniter material (Table 12-9) is typically studied in arc image furnaces or, more recently,[114, 135] with argon ion lasers. The fluences reported are, of course, very much a function of the exposure time and also of pressure. The conductive losses from the mixture, and the kinetics, are directly proportional to the pressure while the corresponding ignition temperature is inversely proportional to the pressure.

Chapter 13

Miscellaneous Ignition Devices

Ignition of Pyrotechnics with Lasers

In recent years, the technology of pyrotechnic ignition with lasers has seen significant advances, especially in reducing the size and energy requirements of devices. It appears that laser initiation is experiencing the kind of enthusiastic reception that electro-explosive devices (EEDs) did a generation ago. The expected benefits are large reduction in mass and cost, compared with EEDs. The use of fiber optics for signal transmission promises a further reduction in cost and mass. The much advertised potential of allowing testing after installation without the need to fire is offset by an increase in complexity.

Laser firing units can be powered either by flash-lamp pumped, solid state lasers or by semiconductor diode lasers. In conventional ignition systems the energy from the firing unit is transmitted to the igniter either by electrical cables or by ordnance transmission lines. Fiber optics are inert, testable, and insensitive to static charges, radio-frequency pulses, and other electromagnetic energy. The initiation mechanism is a thermal one in that the laser pulse heats a spot (in millisecond time frames) on the pyrotechnic substance. The surface may be doped to increase absorption or ignition sensitivity. Auxiliary initiators such as exploding foils or hot wires are not necessary. Shock-induced initiation with Q-switched lasers, while found with explosives, is not observed in pyrotechnics.

A solid state laser consists of a lasing rod (neodymium- or yttrium-doped sapphire) and a condenser discharge-powered (or pyrotechnically fired) flash lamp. The set-up may incorporate a test signal operating at very low intensity. The test signal reflects off a beam splitter and is received in a detector which verifies that the fiber optic line is continuous prior to firing. Typically, the high-voltage capacitor has a volumetric efficiency of about 0.04 J/cm^3. Because the efficiency of the laser is about 2.5%, a typical pyrotechnic initiator requires about 10 J capacity. Recent laser initiation studies of $TiH_x/KClO_4$ and other pyrotechnic mixtures were performed with argon ion lasers[114, 135].

Semiconductor laser diodes are gallium arsenide chips, doped with many parallel "stripes" of trace aluminum. The output wavelength ranges from 88-860 nm. The diode is made to lase by the passage of high currents (>10 A at 20 µs pulse width). The laser diode is more than 30% efficient, but is limited to 10 mJ energy output. The necessary high power density is achieved by optical focusing.

Fiberoptic strands are typically 400 μm in diameter, permitting a limiting power density of 8 J/cm^2. It is customary to drive the diodes at 2.5 times the rated power to achieve the delivery of 20 J/cm^2 per pulse ignoring transmission losses. Operation at high power densities degrades the performance after one pulse.* Continuous wave (CW) laser diodes can have a maximum power output of 1W.*

Table 13-1. Energy Required For Laser Initiation

System	Energy Density, J/cm^2
B-$KClO_4$	0.4
Zr-$KClO_4$	1.2
B-KNO_3	2.4
Ti/$KClO_4$	3.0
Lead azide	3.0
Lead styphnate	1.0
PETN (Zr doped)	9.0
CP†	6.7
CP (Carbon doped)	12
Mg/Teflon	14

† CP= 2-(5-cyanotetrazolato) pentaammino-cobalt (III) perchlorate.

Shock Initiation of Pyrotechnics

Initiation of pyrotechnic mixtures by shock (impact) continues to be poorly understood. Traditionally, initiation sensitivity was measured with drop hammer devices. The lack of reproducibility of the results is notorious and can be traced to the multiplicity in types of test apparatus and of test methods. These were briefly reviewed by J. Roth[72]. Test samples vary in mass and in confinement; drop weights vary in mass and area of working space, and some tests are performed between sheets of sandpaper and some are not.

Walker and Wasley[245] showed that the shock initiation energy could be correlated with the shock initiation energy as derived from the kinetic energy of a flier:

$$E = P^2 \tau \ (\text{cal/cm}^2)^{\S} \qquad \textbf{[13-1]}$$

where P is the shock pressure and τ is the stress duration (pulse width). Stress relief in drop tests takes a long time compared with the duration of a shock wave, and the peak stresses at the initiation threshold in drop tests are much below the pressures in a shock wave. By substituting experimental data into Equation 13-1 it can be shown that there is no difference in shock initiation energy and impact initiation energy. While classic studies on shock initiation thresholds[210] dealt with explosives, the same principles have been found to be applicable to pyrotechnic mixtures as well[105].

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* Spectra Diode Laboratories, 80 Rose Orchard Way, San Jose, CA 95134-1356.

§ More rigorous and dimensionally consistent is the expression: $E = \frac{P^2 \tau}{U_s \rho}$

where U_s and ρ are the shock velocity and the density.

Shock initiation of pyrotechnic mixtures has seen application in donorless through bulkhead initiators (TBIs)[11, 208, 209] which are less sensitive to temperature, shock, and electrostatic discharge than are conventional squibs and detonators. This development has opened the door to the use of pyrotechnic mixtures as end-item devices in explosive trains without the requirement of the usual primers and boosters. Other applications are in the initiation of incendiary devices.

A shock deposits energy into the pyrotechnic mixture by adiabatic compression, by intercrystalline friction, or by viscous heating. Compression causes a temperature rise in the compressed shocked mixture. While explosives react with characteristic kinetics, pyrotechnic reactions are thermal processes. No special initiation mechanisms such as hot spot models[72] need to be invoked to explain the observed results. The ignition sensitivity is enhanced by the porosity,[211] *i.e.*, the low compaction density, indicating that viscous flow or shear banding is a mechanism for initiation.

S. A. Sheffield and A. C. Schwarz[144, 212, 213] and Hardt[105] show that the time frame for this ignition mechanism is in microseconds, or of the same order as a conventional pyrotechnic squib. Relief of the pressure behind the shock wave is not accompanied by a temperature drop, as in a gas, but by attenuation of the shock while the shocked mixture remains hot. The hot zone accelerates the diffusion which starts the reaction. Shock has been shown to initiate diffusion in time scales which are briefer than would be expected from the scale of the original particle sizes. The conclusion is that the initiation mechanism is one of a temperature elevation to the autoignition temperature by shock compression, after which the material reacts in the same way it would if the temperature had been raised by other methods.

The key to determining the shock pressure in the pyrotechnic mixture is the construction of an Hugoniot equation* which, strictly speaking, should be done using experimental data. Inasmuch as Sheffield's and Schwarz's data are at present the only such published Hugoniot equations for pyrotechnic mixtures, it is necessary to rely on a computational scheme for other systems. This was done[97, 104] using the Herman π-α model[111, 211] to construct the constitutive relationships from the Hugoniot equations of the components. It is now possible, by using these techniques, to predict to a first approximation the shock sensitivity of pyrotechnic mixtures, which may be sensitized to any desired degree by the controlled addition of oxidizers or by the control of the compaction density.

The equivalence of shock initiation energy with autoignition enthalpy of reactive mixtures provides a convenient estimate of shock sensitivity from ignition temperatures and heat capacities. Given constitutive properties, *i.e.*, the

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* See glossary.

Hugoniot equations, and heat capacities and autoignition temperature of the pyrotechnic mixture, the shock initiation threshold in terms of shock pressure can be calculated without the need for costly shock initiation experiments.

Ignition of Pyrotechnics using Flueric Matches

Slender cylindrical cavities, with a length to diameter ratio of 30:1, have been shown to exhibit intense heating at the closed end as gas is introduced under pressure[72].

This idea is far from new, having been applied in two British patents of the firearms designer Jean Samuel Pauly, dated 1814 and 1816, covering an "Apparatus for Discharging Firearms by Compressed Air."[195] The concept was revived in the 1960s by Van Langenhoven in a rifle designed to fire caseless .22 caliber ammunition, briefly marketed by Daisy/Heddon.

Incorporation of tapered or stepped cavities gave rise to the flueric match, as shown in Fig. 13-1. When incorporated into a flueric initiation system (one consisting of valving and a gas supply) a flueric match confers potential immunity from the effects of a hostile external environment. Typical experimentally determined endwall temperature-time curves[72], show that the higher the heat capacity of the gas, the shorter the ignition delay. Thus, endwall temperatures of 800° C are attainable in 20 ms when using helium at 50 atm. While flueric initiators were of interest for the ignition of cartridges such as those found in aircrew escape systems, the relatively long ignition delays and system complexity seem to have prevented further development.

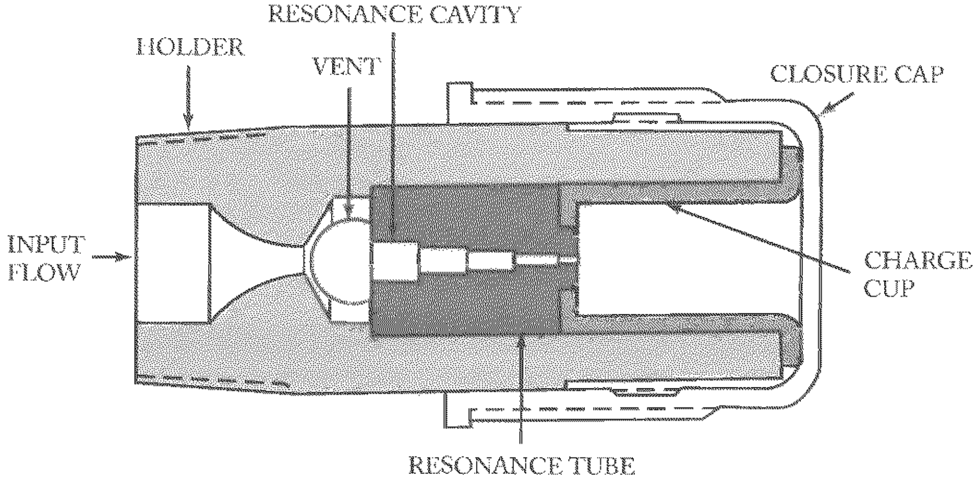

Figure 13-1. Flueric match.[72]

Chapter 14

Miscellaneous Pyrotechnic Effects

Blank Ammunition

The use of blank charges to simulate cannon or small-arms fire for military, ceremonial, theatrical, or other noisemaking purposes is of considerable antiquity. Saluting with blanks has a long history; by the eighteenth century, an elaborate code of military and naval gun salutes had already become firmly established. The practice of using small cannon (known as *chambers* or *codette*) was responsible for one of the world's most famous theater fires, that of the Globe, where many of Shakespeare's plays had their original performances. In a letter dated July 2, 1613, Sir Henry Wotton wrote to his nephew about the fateful performance of *Henry VIII*:

> Now, King Henry making a masque at Cardinal Wolsey's house, and certain chambers being shot off at his entry, some of the paper, or other stuff, wherewith one of them was stopped, did light on the thatch, where being thought at first but an idle smoke, and their eyes more attentive to the show, it kindled inwardly, and ran round like a train, consuming within less than an hour the whole house to the very ground[17].

Music is not without its gunfire, ranging from Tschaikowsky's cannon battery in the *1812 Overture* to the shotgun in Johann Strauss's polka *Auf der Jagd*. Even the rituals of the Church occasionally encompassed the use of blank charges, which were fired (outside the doors) at the Gospel and at the Consecration, in lieu of or in addition to the ringing of bells.*

Blank munitions may be made using black powder, much as they were 400 years ago. A charge (usually equal to – or exceeding – the normal service charge) is confined behind fiber or paper wadding. Upon firing, the wadding is discharged with noise and considerable force from the gun's barrel, but having such small mass, quickly loses velocity and falls to the ground or floor. The procedure for muzzle-loading arms is simply to charge the powder into the barrel, then the wad, to prime and then fire. For use in arms taking fixed cartridges, the powder and wad must fit inside the cartridge case, the wad being secured by means of a sealant or crimp at the mouth of the case to permit the round to be handled without loss of its contents. The finer the grain size of black powder, the louder the report. Usually, FFFg or equivalent is specified. If fiber or card wads designed for the purpose are not available, firmly tamped tissue paper may be substituted in field-expedient situations, and blanks may be made in this manner for almost any firearm for which cartridge cases are available. This suffices to produce a good sound effect, and the visual effect may be more impressive than that of commercial smokeless blanks, on account of the muzzle-flash and smoke. However, care must be taken lest burning paper be evident, spoiling the effect and posing a fire hazard.

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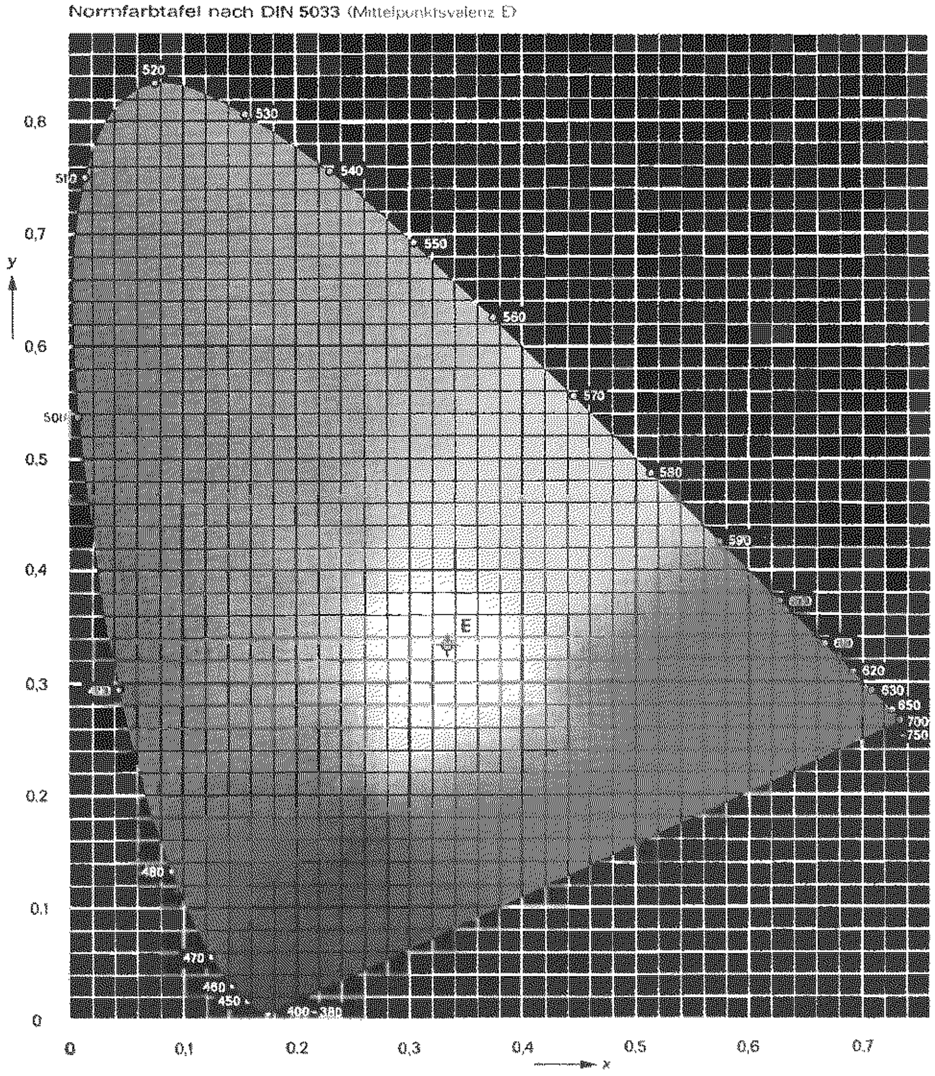
* The practice of firing *codette* during Mass is recreated in a recording of Claudio Monteverdi's *Mass of Thanksgiving*, composed in 1631 to commemorate the deliverance of Venice from the plague (EMI CD No. CDMB-49876, ©1989).

Blanks which contain wadding are hazardous when fired at a person within close range. Serious wounds have often been thus caused, and even death has resulted, either from immediate trauma or from secondary infection, such as tetanus. In the past, injuries from firing of blanks in July Fourth celebrations were common, and being counted together with true fireworks injuries, artificially enlarged the number and seriousness of accidents blamed on consumer fireworks. In recent years, there have been several reported injuries to actors from the misuse of blank ammunition. Persons in such circumstances using blanks should not be presumed to be conversant in general with firearms, much less familiar with the specific hazards of blanks. Proper training would do much to alleviate the risks involved.

The commercial manufacture of blank cartridges is a specialized branch of the ammunition industry. Industrially-produced blanks exhibit considerable sophistication and specialization depending upon the type of weapon and the application for which they are intended. While some blanks are designed for simple noisemaking purposes, others are used in connection with devices or attachments to launch tear-gas canisters, thunder/flash grenades, flares, or other projectiles. A blank cartridge intended to function in a revolver or fixed-breech rifle or shotgun may fail to operate the mechanism of a semi-automatic or automatic arm that is dependent for successful function upon the recoil or gas pressure of a service round carrying the usual projectile. Blanks must be designed especially for particular use in such weapons.

Shotgun blanks are among the few in some cases still commercially made with black powder – notably the 10-gauge 2⅞" blank for use with the Winchester saluting cannon, popular amongst yachtsmen, and 12-gauge blanks for use in field trials and dog training. Smokeless powder is the more usual noisemaking charge, black powder being unpopular with most users due to the necessity of careful gun cleaning after use. Grenade-launching blanks are used by police and military forces in "riot guns" (short-barreled pump or semi-automatic shotguns) to launch tear-gas canisters and thunder/flash grenades. Similar to the shotgun blank is the bird-scaring cartridge, used by farmers to protect crops, which actually contains a small flash salute that, discharged from the gun, bursts in mid-air in a manner comparable to that of an ærial firework salute.

PLATE I



Chromaticity Diagram

PLATE II

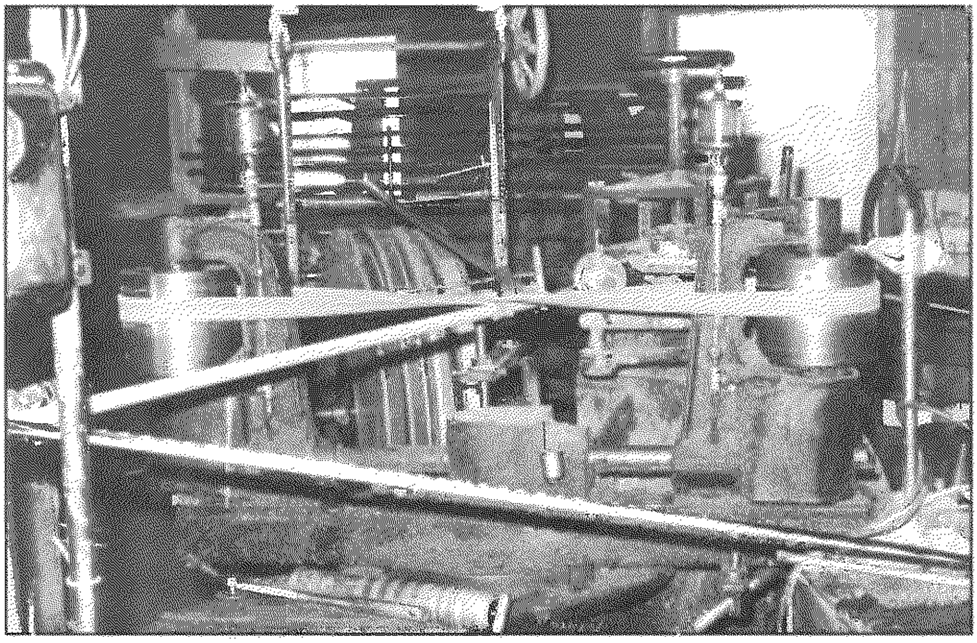


Photo: W.R. Withrow

Photograph 15-1. Spiral tube winding machinery.

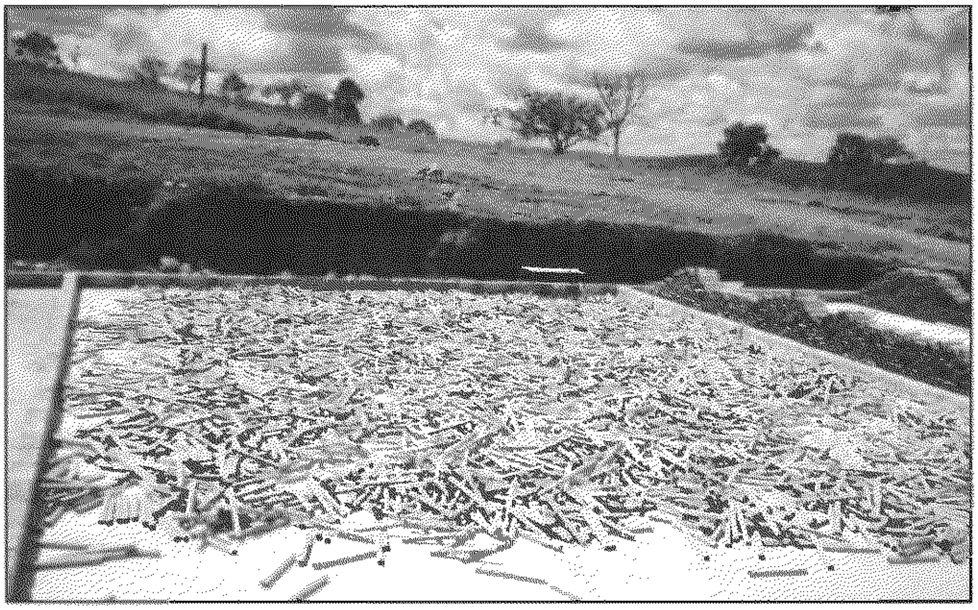


Photo: courtesy Cienfuegos Ltda.

Photograph 15-2. Cases drying in open air.

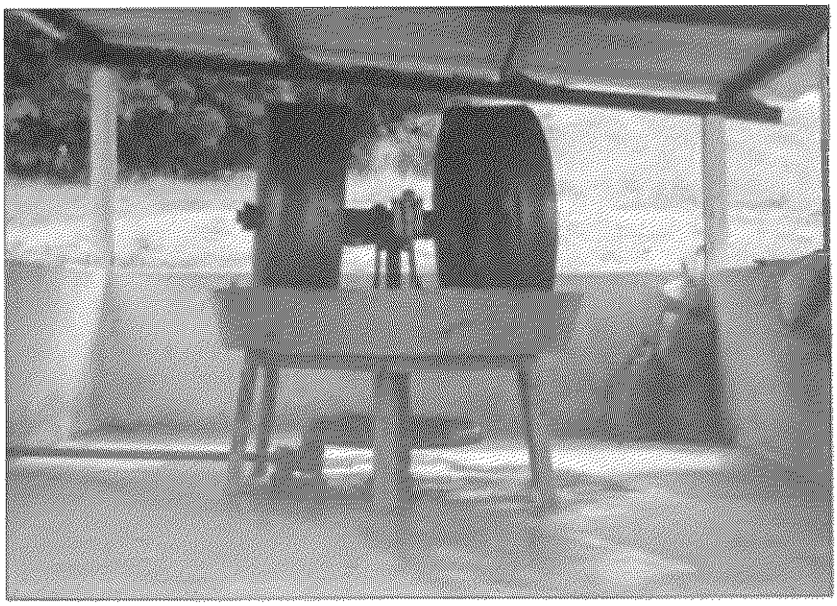


Photo: courtesy Cienfuegos Ltda.

Photograph 15-3. Black powder wheel mill.

Photo: courtesy Cienfuegos Ltda.

Photograph 15-4. Granulated mixture drying on trays.

PLATE IV

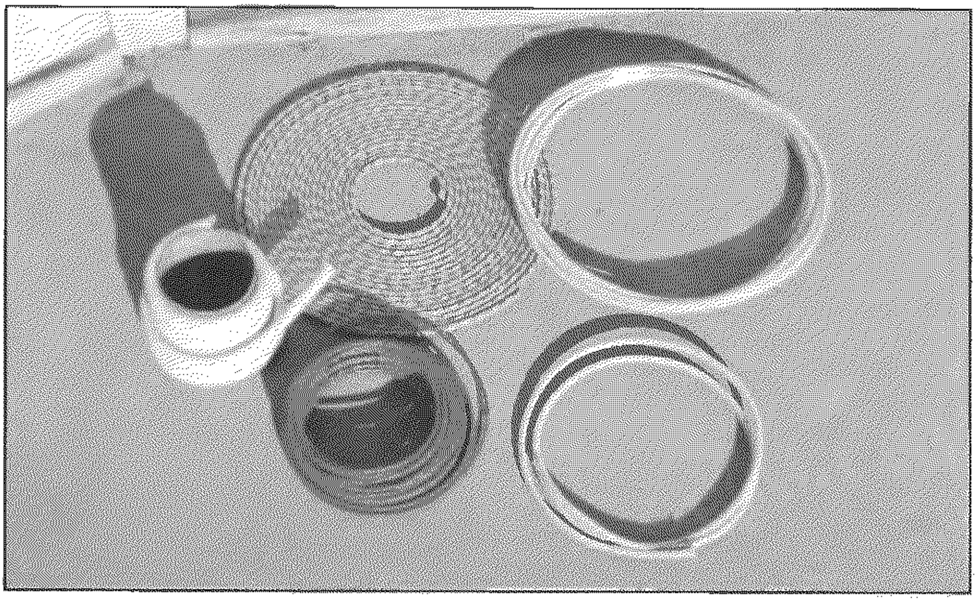


Photo: Barry Bush

Photograph 15-5. Bickford-type fuses. Clockwise from left: 3/8" double-tape fuse for shell timing; 1/4" Japanese time fuse; two types of 1/4" Chinese time fuse; 3/32" red visco fuse.

Photo: Jim Wommack

Photograph 15-6. Fuse-spinning machinery, showing coating baths and drying tunnels (to left).

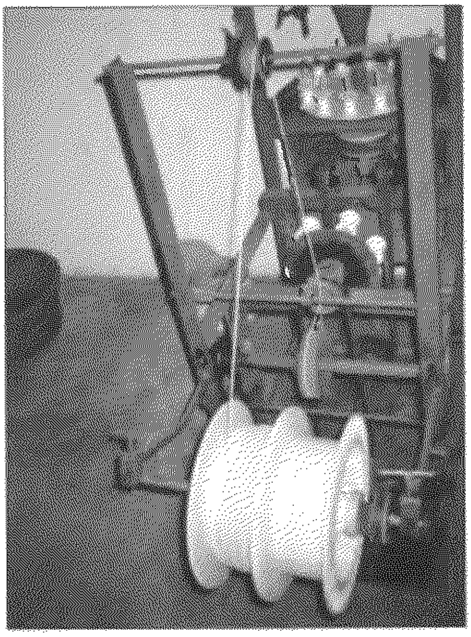


Photo: courtesy Cienfuegos Ltda.

Photograph 15-7. Fuse-spinning machine. This machine does not incorporate in-line coating and drying.

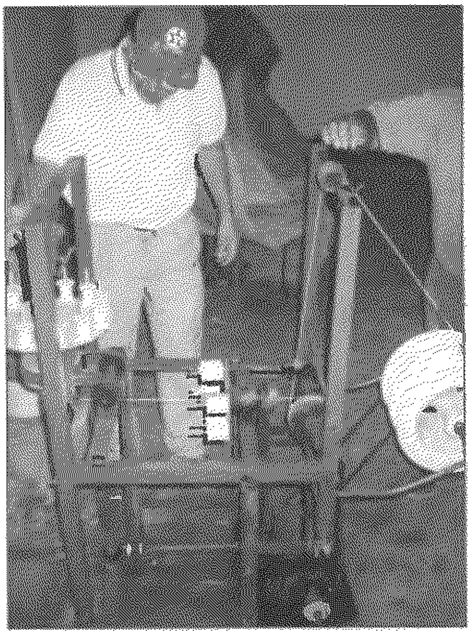


Photo: courtesy Cienfuegos Ltda.

Photograph 15-8. Fuse-spinning machine – side view.

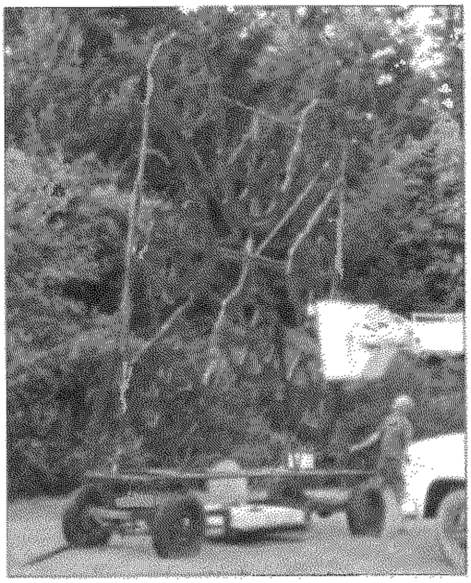


Photo: Ray Anderson

Photograph 15-9. Salamandre *set-piece, as exhibited at Butchart Gardens, Victoria, British Columbia.*

Photo: Emanuel Farrugia

Photograph 15-10. Maltese set-pieces.

PLATE VI

Photo: Alex J. Schuman

Photograph 15-11. Lancework portrait. The subject is Padre Hidalgo. Lancework by FAMSA, Mexico City.

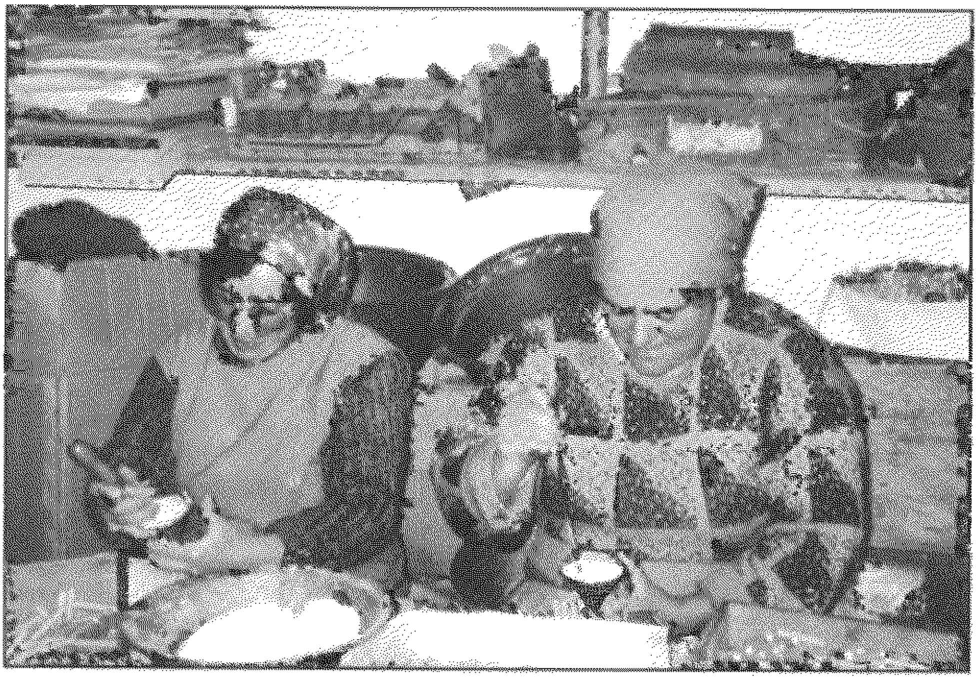


Photo: Lino Nivolo

Photograph 15-12. Funnel-and-wire filling technique.

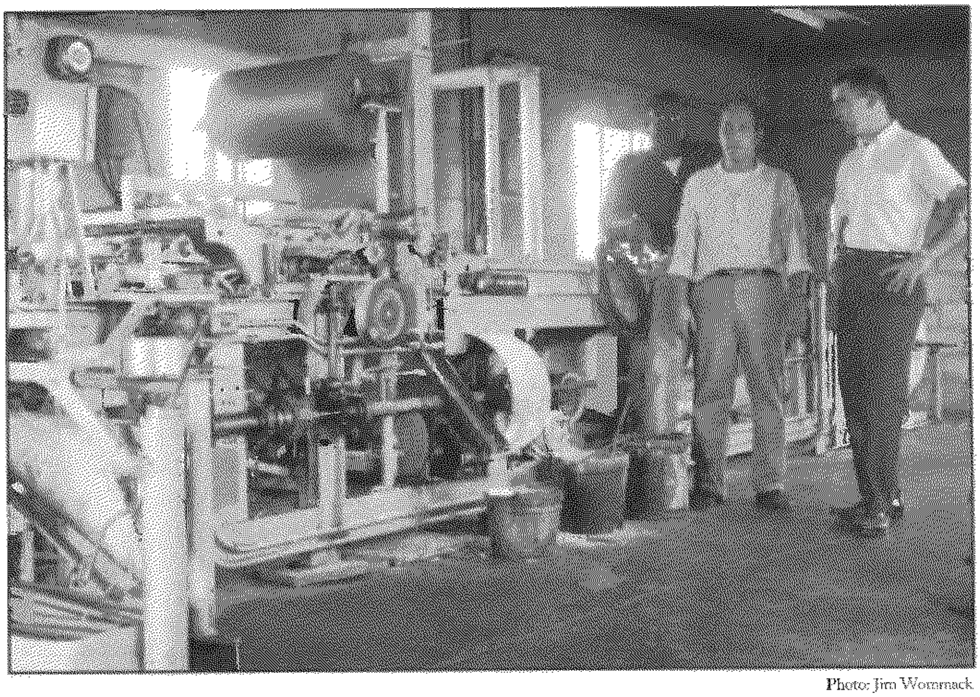


Photo: Jim Wommack

Photograph 15–13. Paper cap manufacture.

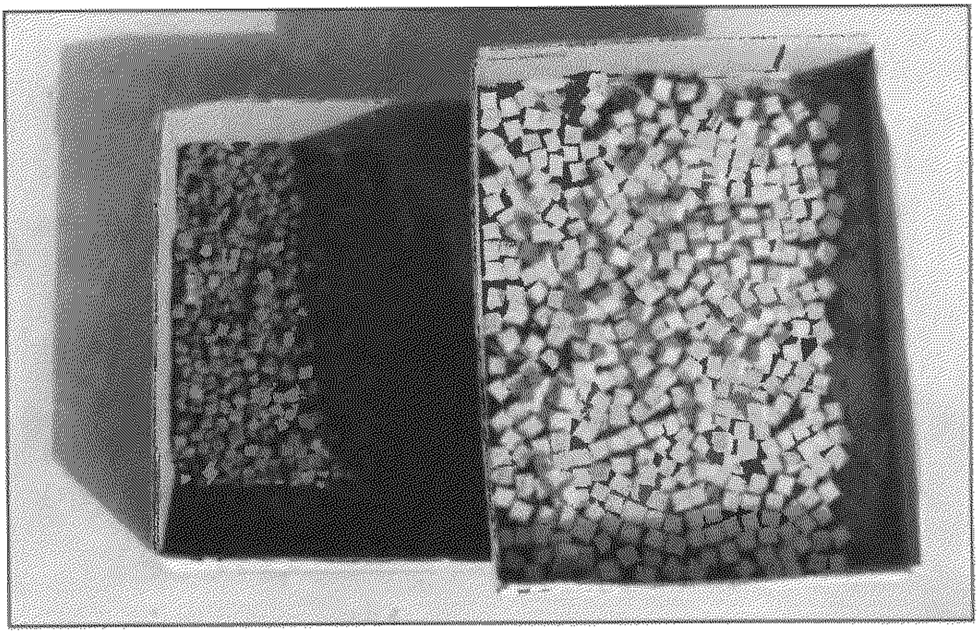


Photo: Barry Bush

Photograph 15–14. Cut stars. The smaller chlorate purple stars have been primed; the saltpeter white stars, containing realgar, have not.

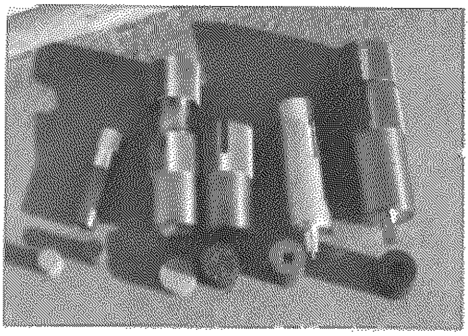


Photo: Barry Bush

Photograph 15-15. Star pumps and pumped stars. Left-right: 1-3, various solid comets, and their pumps (2 and 3 are a set for married comets); 4, crossette with cruciform cavity, and its pump; 5, traditional crossette with round shot hole, and its pump.

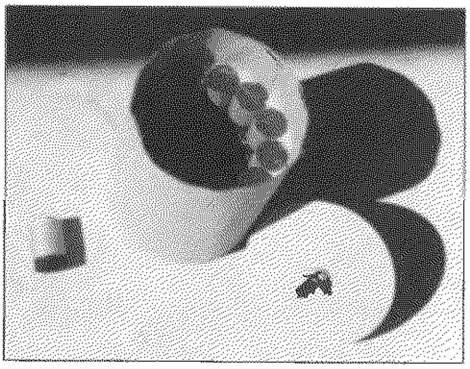


Photo: Barry Bush

Photograph 15-16. Married comet and shell of married comets.

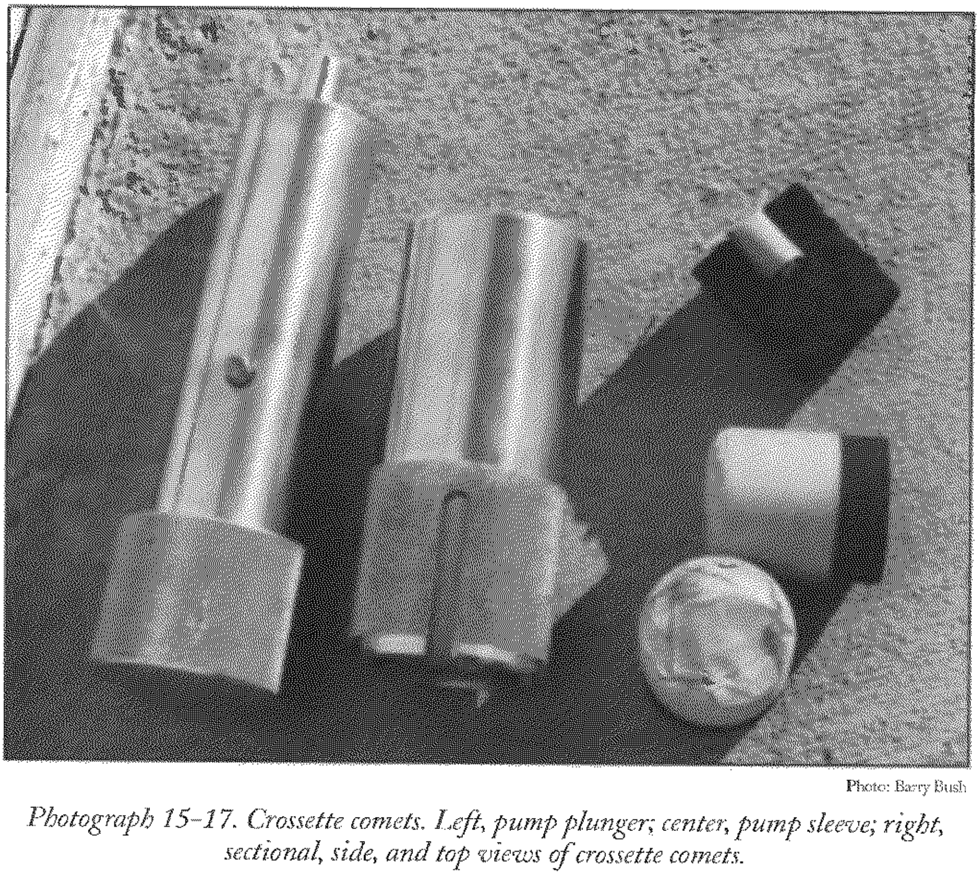


Photo: Barry Bush

Photograph 15-17. Crossette comets. Left, pump plunger; center, pump sleeve; right, sectional, side, and top views of crossette comets.

Pistol blanks may be made with wadding held in a normal-length cartridge by means of a slight constriction or roll crimp at its mouth, or may be made in specially-drawn cases having an extra length of brass "necked down" to the approximate diameter of the projectile ordinarily used, and crimped with a star-crimp or closure in lieu of a wad. The excess brass amounts to a "dummy bullet" that extends the blank round to the length of a normal cartridge and facilitates feed through the weapon's magazine. The crimp is sufficient to confine the powder for production of noise, whilst obviating the necessity of a wad with its attendant danger to person or property. Of particular note is the "5-in-1" blank, the staple of movie and television Westerns. Its "universal" case fits revolvers and rifles chambered in .38/40, .44/40, .44 Special, .44 Magnum, and .45 Colt. The most recent examples are moulded of plastic, the forward end being completely enclosed. The powder charge consists of a smokeless powder, in some instances mixed with flash powder or finely-divided metals to provide greater muzzle-flash, particularly effective in low-light scenes. Reduced loading is sometimes used for greater effectiveness when dialogue is to be heard over the noise.

Rifle blanks have many of the same characteristics that pistol blanks do, but may pose special problems because of their applications. For example, grenade-launching blanks must be loaded to give precise impulse to the grenade with which they are intended to be used. Yet another purpose has been served in some military forces by use of blanks loaded with wooden bullets, and more recently with frangible bullets made of synthetic, non-metallic compositions. These provide necessary recoil and pressure to operate semi- and fully-automatic weapons, while creating little danger to property down-range. The caveats mentioned in conjunction with blanks made with wadding apply, of course, to frangible-bullet rounds, which are fully capable of wounding people or animals fatally. Barnes[15] gives details of numerous types of blanks used in the past and at present by the armed forces of the United States.

Blanks for industrial applications range from .22 rimfire blanks used in rivet-seating tools (larger cartridges may be employed for such purposes) to 10-gauge plastic blank cartridges for use in sounding wells and other seismographic work. Although such blanks have the external form of a firearm cartridge, they are intended to be used in special tools and not in ordinary firearms. They may be chambered in a weapon, but firing may damage the gun and user. Blanks should always be examined to ascertain their appropriateness for the intended use.

Ellern in his earlier work, *Modern Pyrotechnics*,[69] reproduces a formula for a smokeless powder denominated "E.C. Powder." In fact, there were several types of smokeless powders so called, including a special E.C. Blank powder that was formulated to burn extremely fast and hence to give a good report without much confinement. This powder has not been manufactured in many years, and according to Barnes,[15] present-day practice is to use fast-burning shotgun powders of the double-base type, such as Alliant (formerly Hercules) Red Dot. Even so, powders removed from blanks should never be used for reloading ammunition with projectiles, as dangerous pressures may result.

Theatrical Effects

Most theatrical effects, such as smoke, lightning, and flames for stage, motion picture, and television use are not truly pyrotechnic. Pyrotechnics nonetheless has an old and recognized place in theatrical work. Ruggieri,[203] writing in 1810, devoted the fourth section of his *Élémens de pyrotechnie* to "feux d'artifice pour le théâtre." In it, genuinely pyrotechnic devices such as "pluies de feu"* and "courantins"† are described alongside quasi-pyrotechnic effects such as the lycopodium pipe, and non-pyrotechnic flaming effects, *e.g.*, the attachment of pieces of cloth soaked in alcohol to the blades of tinplate swords, the spirits then being ignited to make "flaming swords" for the combats of demons, etc.

After the introduction of potassium chlorate, which made possible the production of true colored pyrotechnic flames, slow-burning colored fire compositions found use in the theater. Mid-nineteenth century publications suggest that this was at one time an application of considerable importance. An example is the use of red fire in the finale of the Gilbert and Sullivan opera *The Sorcerer*. Such use was not without its inconveniences:

> In his autobiography, *The Secrets of a Savoyard*, Sir Henry Lytton tells of an embarrassing incident which once occurred when he was playing Wells and making his final descent: 'One night the trap, having dropped a foot or so, refused to move any further, and there was I, enveloped in smoke and brimstone, poised between earth and elsewhere. So all I could do was to jump back on the boards, make a grimace at the refractory trapdoor, and go off by the ordinary exit. "Hell's full!" shouted an irreverent voice from the gods.'[24]

The advent of electric lighting and the use of colored filters eliminated much of the *raison d'être*, and with it, the 'smoke and brimstone' of theatrical pyrotechnic illumination. Until recently, it was a moribund aspect of pyrotechnics. Its revival is attributable to the rise of the "multi-media" spectacle, as seen in such mass entertainments as rock concerts, professional wrestling "matches," etc., performed in large enclosed spaces such as domed stadia. The effects used are similar to ordinary fireworks (see Chapter 15), with a few exceptions.

Minimization of smoke, especially of a noxious or obnoxious type, is of special concern. Some toxic fireworks ingredients, *e.g.*, those containing antimony, arsenic, or lead, are more easily avoided than are others, *e.g.*, those containing barium. Nitrocellulose, elsewhere significant mainly as a binder, here assumes a special use as a major component of the compositions used in indoor gerbs and line rockets, while fast-burning smokeless powders are used in lieu of black powder to propel miniature comets, mines, and shells from mortars. Alliant (formerly Hercules) Green Dot mixed with strontium or barium chlorides in a ratio, *e.g.*, of 95:5, makes colored flames that are effective and relatively free from smoke. Flash powders used more closely resemble the old-fashioned types employed by photographers prior to the introduction of flash lamps, than those used in military pyrotechnics or display fireworks. They are typically mixtures of strontium or barium nitrates with fine magnesium powder, and are often furnished as two-component sets – oxidizer in one bottle, fuel in another, to be mixed *in situ* – obviating hazard in storage or transportation.

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* Rains of fire, tubes charged with "Chinese fire," and intended to "imitate the fire which falls from heaven by the anger of the gods, or by magic, as in Quinault's *Armide* or Hoffman's *Médée.*"

† Small line rockets.

Unlike the display fireworks industry, which is fragmented and highly competitive, the "proximate" (indoor or stage) pyrotechnic industry is controlled by a handful of companies, which surround their expertise with an air of secrecy, and are not above a certain amount of "hype." One is often led to believe that the compositions used are very exotic or "high-tech," but while a few of the effects are highly specialized, good results are often achieved with mixtures differing little from those used in other fireworks.

Diverging in the early twentieth century from the established practice of the legitimate stage was the fledgling motion picture industry. Pyrotechnics used in motion pictures followed this pattern, taking advantage of the effects derived from "trick photography" (specialized manipulation of the camera and film, or subsequent film editing, including, in recent years, computer simulations). Erupting volcanoes, for example, have been simulated on a miniature scale by dropping glycerine on potassium permaganate,[34] by igniting mixtures of ammonium dichromate, potassium nitrate, and dextrin, or by igniting a gently prepared mixture of potassium chlorate and powdered sugar through the addition of a drop of concentrated sulfuric acid. The ensuing reactions are frequently so violent that visual effects are obtained by filming in slow motion. On the other hand, motion picture "special effects" may involve the ignition of many gallons of gasoline, or the detonation of substantial explosive charges to provide fiery, though not really pyrotechnic, spectacle on a large scale.

A special type of pyrotechnic device is the bullet impact effect which is comprised of electrically initiated igniters or primary explosives* which are concealed within the "targets." Bullet holes as depicted in movies are not technically correct. Normally, when a bullet penetrates an object, it produces an entrance hole of approximately its own diameter, but as it passes through the target, it forces more and more material ahead of it. Upon exit, large chunks of material tear out to form the characteristic exit crater. Usually, for the sake of visual effect, the entrance hole is made to resemble a crater which is then filled with the explosive device, covered with plaster, and painted to conceal the hole. Pyrotechnic devices for theatrical display can be prepared only by specially licensed personnel.

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* Diazondinitrophenol, or "dinol" bullet hits exist for use upon the human body, when mounted on tiny safety armor plates sewn into an actor's clothing. Such a bullet hit will tear a hole and/or break a "blood sack," if desired. A new type of bullet hit is wired to a piezoelectric device which converts the sound from a blank to an electrical signal.

"William Tell" type effects are achieved by attaching black threads to the apple, etc., as few modern performers are as daring or skillful as "Buffalo Bill" Cody or Annie Oakley.

Aerial skywriters use titanium tetrachloride, also known as "liquid smoke." Because it forms hydrogen chloride upon hydrolysis, it is toxic when used in confined spaces. The combination of dry ice and water is usually more effective indoors. These and similar effects are not produced pyrotechnically and will therefore not be examined in further detail.

A number of manufacturers of pyrotechnic devices for special effects are listed in Appendix I in order to discourage the reader from undertaking this hazardous craft.

The Pyrotechnic Laser

At present, the only feasible application of pyrotechnics to laser technology appears to lie in the use of flash compositions, such as potassium perchlorate/zirconium mixtures[126] or zirconium wool in oxygen* to pump neodymium laser rods, for which outputs approaching 10 J are claimed. The principal advantage of pyrotechnic lasers lies in the compactness of the device which may fire mechanically, electrically, or piezoelectrically[259]. The output energy can be transmitted with small energy losses through fiber optics to detonators or photodetectors. Many other schemes have been proposed for pumping the rods pyrochemically, such as by shock-driven gas dynamic reactions[1] but none of these have advanced beyond the conceptual stage.

The use of a pyrotechnic reaction as the source of coherent light is still more speculative. Douda[58] has explored some of the requirements for such chemical lasers. For instance, in an alkaline earth laser, MOH and MCl radicals (where M= Ba or Sr) would be excited above their ground state. The concentration of the excited species is a strong function of temperature. An adiabatic expansion would cause the excitation to decay, bringing about a lasing action. Additional energy could perhaps be pumped into the system from nitrogen or nitric oxide species which can be excited vibrationally to energy levels nearly resonant with the excited molecules of MOH or MCl. Pyrotechnic mixtures may hold promise for laser-initiated ordnance systems. For instance, Maycock[158] showed that those azides, perchlorates, and nitrates which absorb in the long wavelength range in solution are also the most unstable members of the respective classes of salts. Consequently, there is a direct relationship between the absorption spectra of pyrotechnic oxidizers and their respective sensitivities. A study of the decomposition of azides as a source of spectrally discrete pumping energy was published by Dinerman[50].

Commercial Applications

A common application of pyrotechnics is the highway flare, typically composed of strontium nitrate, potassium perchlorate, sulfur, and sawdust with some binder. It burns slowly, leaving a molten residue that prevents excessive ash build-up that might otherwise cause interference with the flame. Similar burning mixtures are found in "gopher bombs," pyrotechnic torches intended to be ignited and thrust into the opening of a burrow in hopes of suffocating these pests.

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* See laser initiation (Chapter 13) and flash cubes (Chapter 17).

Automobile airbag inflaters contain a quick-acting gas generating composition, such as a mixture of potassium nitrate, sodium azide, and silica[178].

For many years, silver iodide or lead iodide was dispersed for cloud seeding. The iodides were combined with ammonium perchlorate in an organic binder, or the iodide could be formed *in situ* by the reaction of lead or silver nitrates with ammonium iodide[214]. In other cases, the iodates of silver or lead were used as oxidizers in conjunction with metallic fuels.

Other types of utilitarian pyrotechnic devices are hand-held rocket signals for use on ships, life boats, and life rafts. These may be parachute flares or signal stars. Similar devices can generate smoke instead of light. Handheld flares can be equipped to ignite by means of a friction-sensitive composition. Other rocket-launched devices are designed to throw life lines.

Model Rocketry

Toy model rocketry has evolved into an interesting hobby and has attained a considerable level of sophistication, partly because the manufacturers support it with journal articles directed at the high-school physics student (THE PHYSICS TEACHER, The American Association of Physics Teachers) and with instruction manuals which cover such subjects as the measurement of ærodynamic drag and the altitude attained by the rockets.*

Model rockets are usually sold as kits with modular, preassembled, solid-propellant engines. These engines are constructed with paper casings, clay nozzles, and compressed black-powder charges which are ignited by a type of electric match. Unlike military solid propellant motors, the burn time, which at most lasts but a few seconds, is brief compared with ascent time. In this circumstance, a combustible confinement is adequate because of the rapid thrust decay. The impulse and thrust can be specified over moderately wide ranges for assembly into single- or multiple-stage rockets. Altitudes of 100 to 1000 meters are claimed, and parachute and camera payloads are available. The concept of prepackaging has added a significant element of safety to what had been a dangerous hobby.

However, as with indoor pyrotechnics, the manufacturers of model rocket engines engage in a certain amount of puffery. The defunct Cox company candidly stated on packages that its engines contained potassium nitrate, sulfur and charcoal, but other makers have always liked to imply that they employ some exotic "space age" technology. Since the 1960s most books on hobby rocketry have been heavily influenced by these companies, and the National Association of Rocketry's safety code was written with their products in mind. Warnings to amateurs which suggest that antiquated black gunpowder is an unacceptable or extremely hazardous material are ironic, considering the amount of it consumed by these manufacturers.

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* Estes Industries, Inc., Box 227, Penrose, CO 81240.

The propellant burns in a manner which is similar to military solid propellants, but delivers only 20-30% of their specific impulse because of the high solid content of the combustion products and the comparatively low chamber pressure[2&3]. The construction of home-made rocket motors with advanced types of propellants was the subject of a recent publication[5]. Details of the methods are beyond the scope of this book and can only be recommended for the serious adult hobbyist. The most popular propellants use a perchlorate oxidizer in combination with a synthetic resin which is both fuel and binder.

Chapter 15

Fireworks[*]

Introductory remarks

Fireworks and pyrotechnics are popularly regarded as synonymous. This identity is even asserted by well-known dictionaries – a cause of some chagrin to those involved in the extensive, technically sophisticated, and diverse industry producing non-firework pyrotechnic articles. Despite its inaccuracy, the common usage persists, probably because fireworks remain the most visible – and spectacular – uses of pyrotechnic phenomena apparent to the ordinary observer.

Historically, the divergence in the development of other pyrotechnic applications from fireworks is recent. A survey of military pyrotechnics published at the end of World War I, Henry B. Faber's *Military Pyrotechnics*[73a], reveals the materials, compositions, and construction techniques for the devices then in use were virtually the same as those used in civilian fireworks, from which they were distinguished only by their packaging and their more limited variety. Differentiation was evident during World War II, as military pyrotechnic articles underwent modification resulting from wartime research and development, and mechanization was underwritten by extensive wartime spending. These trends persisted in the following years, as the Cold War ensued and military preparedness was given high priority. Fireworks, by contrast, remained traditional products, manufactured much as they always had been, but under the added burden of new regulations governing their manufacture, storage, transportation, sale and use. These factors combined to discourage new investment in the firework industry, and hence, the development of new methods and products. Even today it is possible to find fireworks being made in ways that differ little from those in use a century ago, a circumstance that may best be described as a mixed blessing.

According to Ellern[70], in 1960, the total retail value of firework items in the United States then amounted to $16 million, of which about $13 million was domestically produced (81%). McLain[161] indicates that by 1979, total sales were $100 million, but only 25% was domestic. The most recent data, for the year 1999, show sales totalling $625 million. This represented total consumption of 156.9 million pounds, an all-time high surpassing the previous high of 132 million pounds in 1997. Of the 156.9 million pounds, only 6.7 million (4.4%) were fireworks of domestic manufacture.* Allowing for the considerable inflation during this interval, the trends are clear: increasing volumes of fireworks are sold, but domestic production is a steadily declining portion of those sales. Fireworks imported into the United States come overwhelmingly from the Chinese mainland, with much smaller quantities originating in Taiwan, Japan, Brazil, Spain and a few other countries. It is not difficult to discern the reasons for these developments. Fireworks continue to be largely hand-assembled products requiring relatively skilled manual labor. Although a hostile regulatory climate has played its part, it is, at base, almost impossible to compete whilst employing workers who require an hourly compensation that would perhaps buy several days' labor in China.

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[*] This chapter has been written by Barry L. Bush. Thanks are extended to Robert G. Cardwell, Jeremy Clayre, and Michael S. Swisher for additional material furnished.

Fireworks are customarily classified as *terrestrial* (ground-based), *ærial*, and *aquatic*, the last being a traditional category which is now very small. In addition, fireworks for the theater and similar purposes (to which may be added pyrotechnic special effects for motion pictures) form a class by themselves, conveniently summarized under the heading of *indoor* or *proximate* fireworks.

Additionally, fireworks are separated both by custom and by regulation into classes of *display* or *exhibition* fireworks, and *common* or *consumer* fireworks. These may be differently defined and named by the regulations of different countries, but the distinction exists everywhere. In most cases, display fireworks and common fireworks are respectively larger and smaller versions of similar designs, the distinguishing characteristic being a regulatorily-established maximum dimension or pyrotechnic composition content for the consumer article. "Toy" fireworks, such as sparklers, snakes, toy caps, and party poppers, are those types of consumer fireworks for which no corresponding display version exists. These are often the products of specialist manufacturers devoting them their exclusive attention.

It is to be noted that the former terms, "Class B – display fireworks" and "Class C – common fireworks," have been abandoned in U.S. regulatory usage, and replaced by terms drawn from United Nations standards: "1.3G" for display fireworks, and "1.4G" for common fireworks. However, the U.S. regulations setting maximum dimensions and pyrotechnic content for consumer fireworks remain in force; the U.N. standard signified by the designation "1.4G" is actually more lenient and is not applied for domestic regulatory purposes in the United States.[139] The old terms "Class C" and "Class B" are still in common use among people involved with fireworks and cause no confusion. These definitions were originally established by the Interstate Commerce Commission and later came under the authority of the Department of Transportation. As its name implies, this agency is primarily concerned with safety during shipping and storage; until the 1960s the *sale* of fireworks to the public was regulated by the individual states. Class B fireworks, principally large flash crackers, were widely marketed until they were restricted by the Child Protection Act of 1966. Since the early 1970s, the Consumer Product Safety Commission has been involved in the regulation of common fireworks, and a few more changes have been made. More restrictions have been placed on fuses, and firecrackers have been reduced from the earlier Class C limit of two grains (130 mg) to a maximum powder content of 50 milligrams. However, definitions are still set by the D.O.T., and most of the old composition limits and maximum dimensions remain in force.

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* This information was kindly provided by Executive Director Julie Heckman of the American Pyrotechnics Association (APA), the industry's trade association.

In addition to the limits placed on the amount of composition in each item, certain chemicals are restricted in fireworks offered for sale to the public. Compounds of arsenic and mercury are forbidden because of their toxicity; other chemical restrictions are based on fears of excessive reactivity. Chlorates may be used only in a few specific items, and titanium may be included in consumer fireworks only if its particle size is greater than 100 mesh. White phosphorus is banned, and the red form may be used only in caps and party poppers. Other chemicals which are completely excluded are boron, zirconium, unalloyed magnesium, gallic acid and its salts, picric acid and its salts, and thiocyanates.

This chapter will treat fireworks in the order of their traditional categories, terrestrial, ærial and aquatic (considering both display and consumer versions together), with concluding remarks on display practice.

Materials

The major chemicals used in fireworks have been covered in Chapter 16, and more information about them is available in other technical works. Specific chemical preferences as they relate to fireworks will be explained as they arise.

Adhesives, specifically *glue* and *paste*, play an important role in most firework items. White glues based on polyvinyl acetate, such as the familiar brand Elmer's®, are used on paper, wood and other porous materials. Hide glue, stronger and more penetrating, is often a better choice on components such as shell fuses which must withstand high stresses. Historically this type of glue was sold as dry chips or flakes which could be reconstituted with hot water as needed. Today, there is a ready-made hide glue sold for woodworking which is convenient and very satisfactory. Increased use of plastic components has led to the adoption of new adhesives as well. When binding plastic to plastic, especially PVC, the "glue" often is not technically an adhesive at all. Instead it is merely a solvent such as methylene chloride, which dissolves a small amount of the plastic and renders it sticky. The hot-melt glue gun is another innovation which is often used in mass-production of small consumer fireworks. As might be expected, hot-melt adhesives may be dangerous around sensitive compositions. For attaching sticks to rockets or tubes to bases, they are quite useful. Epoxies and other resin glues are not very common in fireworks, but in a few specialized items they may serve as a combination binder and fuel.

Paste is usually made from wheat flour, although other sources of starch can be used. Weingart[249] and earlier authorities give detailed directions for making it, along with preservative methods which range from boiling in a zinc pot to adding powerful antiseptics such as mercuric chloride or phenol. The mercurial is inadvisable, not because of any safety concerns, but because proteins in the flour will bind the mercury and render it relatively useless. Clove oil may be added at the rate of a few drops per quart and normally works very well. Today most pyrotechnists buy a pre-cooked powdered paste intended for wallpaper, which can easily be reconstituted in quantities which will be used in a day or two. Paste is invaluable when working with large pieces of paper, because it permeates the grain well and is not sticky when wet. It also gives a smooth finish and confers some degree of flame resistance after the paper is dry.

Clay is used to plug the ends of tubular casings and to provide reduced diameter nozzles or chokes. Soft granular fire clay is usually preferred, although the dustier bentonite is also commonly used. Plaster of Paris is occasionally used for plugs, either prepared with water in the usual way or rammed dry like clay.

Paper is a very important commodity in firework making. Detailed instructions in older works on pyrotechny often prove frustrating when they call for types of paper which are obsolete. Similarly, hobbyists often find that grades of paper which are adequate for small devices are not suitable when they progress to larger ones. In general the "gold standard" is brown kraft (sulfate process) paper, familiar as wrapping paper for parcels. This material takes paste well, is durable when wet and very tough after drying. It must not be confused with recycled or "bogus" kraft, which easily comes apart when dampened. The "weight" designation of kraft, based on the weight of a ream of a standard size of paper, corresponds roughly to its thickness in ten-thousandths of an inch. Thus "30-pound kraft" is about 0.003" thick, while "70-pound" measures approximately 0.007". Many other types of paper, from chipboard sheets to thin tissue, are used in fireworks. While standard grades of industrially-produced paper account for the great majority used in firework manufacture in all countries, several varieties not seen in the United States are occasionally observed elsewhere. Japanese handmade papers have the virtue of random orientation of the fiber, and hence do not exhibit the pronounced "grain" of the machine-made product, in which the fiber is directionally aligned as a consequence of the manufacturing process. This "grainless" property renders hand-made *gampi* tissue especially suitable for flags, parachutes, and the like, because of its resistance to becoming set in folds. Similarly, tough *kozo* paper is valued in shell-making because its tensile strength is equal in both directions. Occidentals sometimes mistakenly refer to these as "rice papers" but in fact they are made from other plant fibers.[216] A coarse, unsized paper is found in Chinese firecrackers, and this too is often hand-made, not because of any specially desirable properties, but merely because primitive conditions and abundant manual labor make it the cheapest available type. Strawboard, referred to by Weingart[249], has been replaced in the United States by chipboard, but is still encountered in Asian and some European manufacture. Fireworks intended for sale to the public are of course finished with colored papers and decorative printed labels.

Case rolling (Photos 15-1 and 15-2) is a specialty unto itself, and today it is mostly done by machine. Until the twentieth century almost all cases were parallel wound, made by rolling long strips of paper around cylindrical formers.

Dry-rolled casings, pasted only on the last turn of paper, were used in crackers and in thin-walled items such as torches. More common were wet-rolled casings with paste all the way through. Machine-made parallel tubes are all wet-rolled, from various grades of brown paper; virgin kraft is preferable for devices which generate high pressures such as rockets, tourbillions and hummers. Spiral-wound tubes, also rolled by machine, have become very common in pyrotechnics. In a given size, they are not as strong as parallel-wound tubes, but are significantly less expensive and are adequate for lower-pressure devices.

Cardboard discs are used on ends of cylinder shells and similar devices. Many standard sizes are manufactured by diecutting on presses. They are typically made of chipboard about ⅛" thick, although thinner ones may be used for special purposes. Stronger discs of kraft paper are also sold, but are more expensive than chipboard.

Paper *cup sets* are usually kraft of about .030"-.050" thickness and are punched out by dies. When properly made they can be assembled to form small casings that are roughly spherical, and these become more rounded after a suitable coating process. Cup sets have been used to make the notorious "cherry bombs," as well as smoke devices and even miniature star shells. Paper *end plugs* and *end caps* are quite similar, but are sized to fit specific tubes, either on the insides or the outsides.

Shell hemispheres are available for making spherical bombshells, and are typically ⅛" to ¼" thick depending on size. They are sold, suitably undersized, for all the standard calibers of shells from 3-inch to 12-inch, and are intended to be built up to final diameter by repeated wrapping with pasted paper. The Japanese ones in particular are very regular in size and have even edges which mate to produce smooth joints. Plastic hemisphere sets are currently popular, and other types of plastic fireworks casings are also on the market.

Twine is important for many purposes in pyrotechny, ranging from the simple tying of a fuse into a paper nosing to the reinforcement of large complicated ærial shells. Cotton twine is the usual choice; the more expensive but much stronger linen also remains in use among traditionalists. Typical sizes are 8-ply and 12-ply cotton, and 2-, 3-, and 4-ply linen. Aside from the different strengths, the "plies" of the two fibers are different sizes, so that for example, 3-ply flax is about the same diameter as 12-ply cotton and has a much higher breaking strain.

Black powder (Photo 15-3) is the backbone of the fireworks industry and it is involved, in one way or another, in all but a handful of devices. Many aspects of its manufacture, safety considerations and burning characteristics have been covered elsewhere in this book. The characteristics of commercial powder vary somewhat from one manufacturer to another, but the granulation is usually designated by using the letter "F," with more Fs indicating finer granulations. In the United States the old DuPont sizes have been carried over to the current Goex product. The composition of this firm's firework or blasting powder appears to be the same as that of its sporting powder, but the firework grades are usually unglazed and have a much larger variation in grain size. *FFA* resembles fine black gravel; it passes a 4-mesh sieve and is retained on 12 mesh. This powder is a staple of the industry and is used to burst shells and rocket headings, and as a lifting charge for projectiles ranging from small comet stars to twelve-inch spherical bombs. Obviously this ubiquitous "two-F" must not be confused with the FFg black sporting powder used in rifles and shotguns, which is a much finer granulation. FA powder, even coarser than FFA, is sometimes used to lift long, heavy cylindrical shells, but in normal commercial practice FFA is all that is required. FFFFA and FFFFFA powders are similar in particle size to sporting black powders. 4FA is the more common of these, and is often preferred as the lifting charge for small shells and Roman candle stars, as well as for bursting charges. 7FA, the same granulation as 4Fg sporting powder, is the finest grain powder normally offered. It finds some use in priming, and is also mixed into compositions for fountains and similar tube items. The "A" in all these designations (distinguishing powder made using potassium nitrate) is a survival of the days when a grade "B" black powder, made from sodium nitrate, was in common use for blasting coal and soft rock.

Meal powder is a very important commodity in the firework world. The commercial product comprises the fine dusty material left over after screening the different sizes of grain powder. Since it has been through the complete process of milling, pressing and crushing, true meal powder represents a far more intimate mixture than could be obtained merely by passing saltpeter, charcoal and sulfur through a sieve. *Meal D* consists of particles 40 mesh and finer, and is widely used in fuses, fountains, gerbs, wheel drivers, spinning devices, rockets, stars, and priming. Fine and extra-fine meal powders are also offered. Because they are bulkier and messier to handle, they are not commonly used in compositions to be rammed in tubes. However, some pyrotechnists prefer these very fine powders for priming stars. Although it is not usually available in the United States, powder mills in some countries produce a *sulfurless meal*, containing approximately 70% saltpeter and 30% charcoal. This product is primarily used for priming stars which contain ingredients that might create a greater hazard in contact with sulfur, such as chlorates or magnesium powder.

Commercially milled black powder is relatively expensive, and its fast burning rate is not always desirable; thus most firework makers produce their own slower meal powder as well. Typically the three ingredients are charged into a cylindrical container with balls of lead, bronze or other non-sparking material and the container is revolved by mechanical means for several hours. Often a small percentage of a water-soluble binder such as dextrin is added, so that the finished powder will be ready for use as priming, or for granulation by a wet process. Care and cleanliness are important in this operation, because many of the chemicals used in fireworks would be very hazardous in a ball mill. However, when used only with black powder ingredients, the process has a good safety record. Many compositions for fountains and tailed stars produce impeccable results with such cheap "homemade" powders. Others definitely perform better with the more energetic commercial Meal D. Often it is necessary to make experimental trials to determine whether the price difference is justified.

Few if any firework manufacturers go to the trouble of subjecting ball-milled powder to hydraulic pressure, and then breaking up the cakes as gunpowder mills do. However, wet processes are often used to make special types of granulated powder which are used in ærial shells and other large pieces of fireworks. The usual "rough powder," or *polverone* is made from black powder ingredients with the addition of about 5% dextrin as a binder. The proportion of the other ingredients varies slightly; there is often a lower oxidizer content than in commercial gunpowder. The composition is not normally milled, but is mixed by passing it through screens. The addition of water, often hot, incorporates the ingredients further but is primarily a means of forming the powder into granules. At approximately 20% water content the mixture is pliable enough to be formed by hand into masses resembling meat patties or black snowballs. It is then rubbed through a coarse screen of about 4 mesh; 4 × 4 galvanized "hardware cloth" is readily available and is in common use for this purpose. The resultant granulated material is caught on screen-bottomed trays lined with sheets of paper (Photo 15-4); if desired, it may be gently rescreened while still moist to eliminate any large clumps. When the powder is dry it is usually shaken on finer screening, like that used for windows, to sort out dust.

Rough Powder (Polverone)

Potassium nitrate	67	64.5
Charcoal, air float	16	16
Sulfur	11	13
Dextrin	6	6.5

The dust may be used for priming or other purposes, or it can simply be passed through the process again. Many manufacturers sift their polverone into different grades, for example 4 to 8 mesh and 8 to 20 mesh, for use in different sized fireworks. Such powders burn much more slowly than commercial milled powders, and are less powerful, but their use is not only as a means of saving money. In some cases they are chosen where a gentle burst is desirable, and they may be combined with commercial powder or other materials to give a wide variety of power levels. Polverone has special significance in the Italian style of cylindrical bombshells, where it may be described as a combustible filler material. Other burst powders, including chlorate and perchlorate mixtures that would not be safe to mill, can be granulated by the same type of wet process.

Many types of fuse are used in fireworks, both as timing devices and to insure positive function. Metallized "igniter cords" designed for blasting operations have seen rather extensive use in recent decades, but firework applications are not sanctioned by the manufacturers of the cord, and its availability is sporadic. *Slow match* is simply cotton cord impregnated with saltpeter or another nitrate oxidizer, and is rarely seen today. It was seldom used as a fuse, rather being a source of fire to ignite other fuses or powder trains, somewhat like a punk. Also uncommon today is *touch paper*, tissue paper (typically blue in color) dampened with a solution of saltpeter, then dried. This was formerly wrapped around the tops of certain consumer fireworks like small fountains and torches.

All the commonly used types of fuse depend on black powder in one form or another. *Quickmatch* has many applications and is practically essential for non-electrical firing of large displays. Even where electrical igniters are used, it is still important for internal components of wheels, shells and other complex fireworks. Match is produced by soaking soft, unbraided cotton cord in a slurry of black powder and water, which contains a small percentage of an adhesive such as dextrin, starch, or gum arabic. In practice the best match is made with commercial meal or fine grain powder, which is easily reduced to a paste when hot water is added. Five to fifteen parallel strands of small twine may be used, and the product is drawn through a simple die – often the spout of a small funnel – to strip off the excess powder slurry and to help give the match a rounder shape. It is then wound on a frame, where it is optionally dusted with more meal powder, and allowed to dry.

Good match is quite dense and stiff, yet may be bent double without losing much of its coating. When cut cleanly across the end it ought to show black all the way to the center of the bundle of cotton strands. Its normal diameter is at least ⅛ inch, but smaller sizes are made for special applications. In the open air without wind it burns about two to four inches per second with a great deal of flame.

When match is encased in a loose-fitting paper tube about ¼ inch in diameter, the containment of hot gases causes the reaction front to travel far more rapidly. Published figures for its speed range from twenty feet per second to more than one hundred. This phenomenon makes an impressive demonstration for anyone unfamiliar with the properties of black powder and fireworks. Piped match with its nearly instantaneous transfer of fire is most commonly seen as the "leaders" of ærial shells, which are ignited from the muzzles of their mortars. It is used in connecting long series of shells used in the finales of large public displays, and it plays a part in many other devices such as lancework and wheels. Some pyrotechnists have taken to using the term "quickmatch" only for the type with a paper covering, and call the bare version "black match." More traditionally, quickmatch is the general term, and this is further categorized as bare or piped, as the literature[70, 128], and the most recent Department of Defense specification for this article, MIL-Q-378B, both make clear.

As with most products, quickmatch has a hierarchy of quality, and some of it is quite frankly of a low grade. Owing to the cost of commercial powder, it is often made with homemade meal or "scratch mix" which varies greatly in quality. In some cases this is easily detected because the match is pale grey in color, and yellow particles of sulfur are actually visible to the naked eye! Also, the piping on commercial bundle match is rather flimsy, machine-made tube which is not nearly as strong as hand-rolled kraft piping. Most commercial match is perfectly adequate for connecting lances or finale shells, but is not the best choice for leaders or passfires on large heavy shells. The same can be said of much match imported from Asian manufacturers, which tends to be very fast burning but often consists of several separate strands and tends to have low physical strength.

Bare match is sometimes surrounded by compacted clay or sawdust in devices used inside rockets or shells (*q.v.*). This technique gives very reliable ignition and useful, though not precise, delays. Many consumer fireworks, such as fountains and Roman candles were formerly fused with bare match. Consumer safety regulations, which among other things require a delay of 3 to 6 seconds before ignition, have made this practice obsolete in the United States.

The Japanese manufacture an ignition medium used in a similar fashion to bare match, somewhat intermediate between it and the touch-paper mentioned earlier. This is *powder-pasted paper,* made by coating strong Japanese tissue with black powder slurry. Upon drying, it may be used for a variety of ignition purposes, as well as the manufacture of traditional Japanese shell fuse[216].

Bickford's *safety fuse* was developed in 1831 for use by miners, and the product was manufactured by the original firm until about 1970[68]. Today many similar brands of safety fuse are available. All are made on machines, resembling those of Bickford's original design, which twist yarns around a black powder core. The product is then coated with asphalt, which in turn is covered with cloth or paper and sometimes additional threads. The burning rate is usually around 30 seconds per foot, although it does vary from brand to brand. Two types of ¼-inch Chinese fuse are commonly sold, the one with all white threads being slower than the kind which also has red threads. Some Chinese shell leaders resemble a safety fuse with multi-colored threads; obviously substitution could be disastrous! A Japanese fuse, reputedly made by Hosoya, is identifiable by its two white threads alternating with two red threads over a tan paper wrapping. It is considered more consistent in timing than the Chinese brands, but is also much more expensive. Common blasting or "dynamite" fuse, approximately ¼-inch in diameter and typically coated with orange wax, has a slightly slower burning rate than do the types intended for fireworks. Because of this, and also because its waxy surface does not bond well with glue or paste, it is not well-suited as a shell fuse, but it occasionally finds use as a delay element in set-piece and finale work. A high-quality ⅜-inch time fuse is made by Newco of Cincinnati, Ohio, specifically for fireworks use; it has a white cloth covering. All of these fuses are convenient and reliable, and have the advantage of being virtually impossible to ignite from the side (Photo 15-5). Indeed they are not always easy to ignite from the ends, and they need to be primed. Black powder slurry much like that used for quickmatch may be smeared on the end and sprinkled with grain powder. In this application a non-aqueous binder (such as nitrocellulose lacquer) is often preferred so that water does not leach into the fuse core. In another method, called "cross-matching," a hole is punched through the time fuse and is threaded with small-diameter, high-quality bare match. This technique is very reliable but requires more skill than slurry priming.

A small-diameter spun safety fuse, without the asphalt layer, is extensively used in fireworks sold to the public (Photos 15-5, 15-6, 15-7, and 15-8). It is often called "visco" after the lacquer used to coat it, and is available in red and green, and sometimes other colors. It will burn under water but is not waterproof on long immersion like the other Bickford types. Visco is much less expensive than the larger time fuses and is easier to ignite with a match or cigarette lighter, but it still has some resistance to ignition from the side.

The Chinese traditionally make small fuses about 1/16" diameter from tissue paper and meal powder, which will be familiar to any reader who has purchased firecrackers. In the United States in 1995 the Consumer Product Safety Commission (CPSC) banned this type of fuse for bottle rockets and many other small fireworks. It is difficult to see what the fuss was about, since most of these items are too small to cause serious injury even if they do ignite early. Good tissue paper fuse is actually preferable to much of the low-quality visco which the Chinese have since rushed to produce.

Terrestrial Fireworks

Colored Fires, Torches, and Lancework

The simplest form of firework consists of loose powder which can be burned on the ground, on a tile or in a pan to produce colored flame. Called "tableau fire," such mixtures were formerly sold in small boxes or cans. They were popular enough that they were sometimes prepared by pharmacists, when drugstores carried much larger inventories of raw chemicals than they do today. Users were often directed to press the powder into a wineglass or similar container, and to invert this leaving a conical pile of powder. Usually it is desirable to have a composition which burns as slowly as possible without going out or producing excessive amounts of residue. Thus although tableau fires are chemically related to colored stars, they rarely contain the most reactive fuels such as charcoal or metal powders, and the ingredients may be more coarsely ground. White fires, and sometimes yellow, gold or pink, may be made with nitrate oxidizers only. Other colors contain chlorates or perchlorates, although potassium chlorate content is usually kept to a minimum to avoid increasing the burning rate.

The procedure for mixing simple colored fires is the same as that used for most other pyrotechnic compositions. Today oxidizers are usually purchased as fine powders, but some tend to agglomerate into hard lumps on storage. Saltpeter and potassium chlorate are bad in this respect, and barium nitrate is even worse. Usually the oxidizer alone should be rubbed through a fine sieve of 40 to 60 mesh before it is mixed with the other ingredients. In some cases the oxidizer alone may be ground in a clean ball mill, passed through a hammer mill, or placed in a canvas or leather bag and beaten with a mallet to break up lumps. After the powdered oxidizer is added to the other ingredients the mixture may be passed three or four times through a 20 to 30 mesh sieve. This process generates potentially hazardous dusts; workers need to wear masks and the mixing should be done outdoors or in special sheds separated from other operations. For most purposes it is not desirable to mix chlorates with sulfur or sulfides, and in some countries such mixtures are prohibited by law. Therefore separate sieves and mixing areas usually are employed for the two classes of compositions. Ammonium perchlorate is particularly incompatible with chlorates, because if the mixture becomes wet it is likely to form dangerously unstable ammonium chlorate.

Table 15-1. Tableau Fires

	Red	Green	White	Yellow
Strontium nitrate	69	-	-	-
Potassium chlorate	11	-	-	9
Barium nitrate	-	16	-	69
Barium chlorate	-	65	-	-
Potassium nitrate	-	-	67	-
Red gum	11	5.5	-	15
Sodium oxalate	-	-	-	7
Antimony sulfide	-	-	22	-
Sulfur	-	-	11	-
Charcoal, air-floated dust	3	1.5	-	-
Wood meal	6	12	-	-

NOTE: All compositions in this book are given in mass percentages, with rounding as appropriate, to facilitate comparison; it is worth noting that most fireworks makers actually mix in simple "parts by weight" to produce batches of convenient size. For example, the white fire in Table 15-1 was originally 6 pounds of potassium nitrate, 2 pounds of antimony sulfide, and 1 pound of sulfur.

Furthermore, ammonium perchlorate tends to attack brass, so compositions containing it are best mixed with dedicated sieves of stainless steel or Monel metal. If tableau fires were more popular today they would be ideal applications for ammonium perchlorate compositions, which can produce very good colors with minimal smoke. Some of the disadvantages of ammonium perchlorate, such as its sluggish ignition and its incompatibility with black powder priming, would not be an issue with loose powders. However, for a variety of reasons tableau fires are far less common than they once were. Theatrical lighting is now done mostly with electricity. Shipping regulations, together with rules limiting the amount of compositions in each piece of consumer fireworks, have had a negative impact on the use of colored fires in backyard displays. Color compositions burn more efficiently, and can be stored more safely, in the form of flares or torches.

The pyrotechnic torch is familiar to anyone who has examined a red safety flare or fusee. This item consists of a waxed, spiral-wound tube of about 7/8" inside diameter, with the composition packed firmly inside but not rammed into a hard cake. A wooden plug with a handle or metal spike closes the bottom of the flare, while the top is primed for ignition.

Red Railroad Flare (Fusee)[70]

Strontium nitrate	74
Potassium perchlorate	6
Sulfur	10
Paraffin wax or petrolatum	2-6
Fine sawdust	8-4

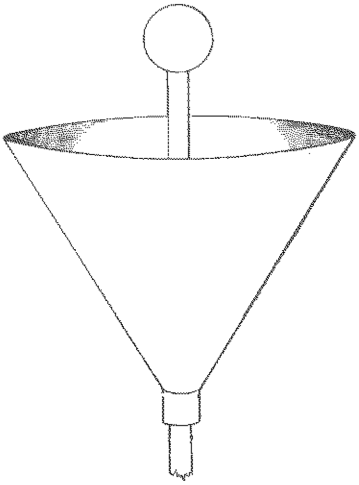

Figure 15-1. Funnel and wire.

The paraffin wax or petrolatum is dissolved in mineral spirits, and the resultant solution is used to dampen the composition. The cases are mechanically charged.

Many torches (including the common road flares) feature what is really a giant safety match head, and are fitted with a cap which has a match striker composition on its outer surface. To ignite the flare, an outer wrapper must be removed, after which the cap can be inverted and scratched against the bead of ignition mixture. Torches intended for display rather than signalling usually do not have this type of ignition system; instead they are fitted with visco fuse or bare match, or even a simple bead of priming which must be ignited with a match or other flame source. As a rule, the casings of these items are strong enough only to withstand normal handling and shipping stresses. Having them too thick is counterproductive and interferes with flame production. Many torch or flare compositions have a slight excess of oxidizer which helps burn away the paper as the reaction proceeds; in the ordinary red fusee, the strontium nitrate fulfills this role, and the hot molten dross produced is not usually a problem because the device is not held in the hand. Hand-held parade torches were once a popular piece of fireworks in the United States. Because the dangerous dross had to be kept to a minimum, these torches required carefully designed compositions, and were usually more expensive and of shorter duration than safety flares. They are rarely seen today, but in Britain and continental Europe, firework displays still feature colored "bengal" flares that are burned on the ground.

Portfires, though they have largely been replaced by the common red railroad fusee (*vide supra*), are still occasionally used for igniting other pieces of fireworks during a display. They are small torches about ⅜" in diameter, filled by funnel and wire (Fig. 15-1), and typically burn 7-10 minutes. They are usually made with a saltpeter white fire or other nitrate composition, for example:

Portfire

Potassium nitrate	57
Sulfur	16
Barium nitrate	16
Antimony sulfide	5
Meal powder	1
Wood meal	5

Burning time can be adjusted by varying the content of wood meal.

Lances (Tables 15-2, 15-3, and 15-4) are nothing more than small colored flares, slightly larger than cigarettes. They have no handles, but are closed with a simple paper fold at the bottoms and are primed at the tips with black powder slurry. Typically they are around four inches long and burn for one minute; part of the art of making good ones is to formulate the different colors to burn with approximately the same duration. Lances are used in large quantities to spell words and to draw pictures or geometric designs on wooden frames. It is convenient to drive double-ended nails into these frames, on which the lances may be impaled as needed. Once a design is completed, the lances are connected with piped match, which is attached to each individual lance with tape or pasted paper, and often with a pin as well.

In Japan, many manufacturers make the picture's/word's frame out of flat wooden slats and then use lances with half the tube flattened. These are attached using a staple gun. The lances are also equipped with a piece of visco-style fuse cemented into, and protruding from, the lance prime. Matching the tubes to burn in unison is therefore a simple task of passing around quickmatch, and twisting the visco-style fuse around it. This method may be particularly adaptable to words in the Japanese language, as steeply curved *ji* are less common than steeply curved letters in the Roman alphabet.

Lancework may be combined with many other types of fireworks to form elaborate ground displays, and the pictures can be made to move by pyrotechnic or mechanical means. One such classic design is the *salamandre*, or snake-and-butterfly, which Ruggieri[203], writing in 1810, claimed as an invention of his family's, and which is still occasionally exhibited (Photo 15-9). In Malta, large geometrically-patterned lancework pieces, animated by wheel drivers and connected with universal joints, have been brought to the height of sophistication (Photo 15-10). They were called to the attention of the worldwide fireworks community in 1981[75], and have since been copied (with varying degrees of success) in other countries. Brock[26] describes "living fireworks" – men clad in fireproof suits adorned with lancework, performing various actions as the lances burnt. Large portraits (Photo 15-11) and landscape scenes hundreds of feet long were once common, especially in Britain and on the European continent. Today's set pieces are rarely so extravagant, but lancework is still seen in conjunction with ærial displays, where it can represent a flag or a company emblem, or spell messages such as "GOOD NIGHT." It has even been used in television advertising, in the form of corporate symbols or sales slogans. The loud roar and wall of flame produced

Table 15-2. Red and Blue Lance Compositions.

	Red			Blue		
	1	2	3	4	5	6
Potassium chlorate	67	-	-	63	-	-
Potassium perchlorate	-	62	35	-	70	27
Ammonium perchlorate	-	-	30	-	-	47
Strontium carbonate	22	21	17	-	-	-
Paris green	-	-	-	29	-	-
Black copper oxide	-	-	-	-	12	-
Basic copper carbonate	-	-	-	-	-	11
Red gum	11	14	10	-	-	15
Stearin	-	-	-	4	-	-
Asphaltum	-	3	-	-	-	-
Hexamine	-	-	4	-	-	-
Hexachlorobenzene	-	-	-	4	-	-
Polyvinyl chloride	-	-	-	-	18	-
Dextrin	-	-	4	-	-	-

NOTES: Formula 3[16], the ammonium perchlorate red, and Formula 6[139], the ammonium perchlorate blue lance compositions, require a special prime (Formula 4, Table 15-4). Being incompatible with nitrates because of the possibility of hygroscopic ammonium nitrate forming through double decomposition of potassium nitrate and ammonium perchlorate, they cannot be used in conjunction with nitrate primes nor with the 'dead lance' composition (Formula 5, Table 15-4).

by large quantities of quickmatch easily grabs an audience's attention, and is almost as memorable as the fire picture itself.

Color-changing lances are sometimes used to produce transformation designs; these are essentially custom projects which may be made by firework companies for special exhibitions. Naturally, care must be taken to avoid potentially dangerous situations, such as having a chlorate composition in direct contact with one containing ammonium salts, which might cause spontaneous ignition if left for a long period of time in a damp climate. One interesting mixture which has been used in this type of work is the "stop," "dead," or "dark" lance composition. An example is given in Formula 5, Table 15-4. With such a large excess of strontium carbonate, which is neither fuel nor oxidizer, this mixture does not produce a luminous red flame; instead, it smolders with almost no flame at all. This phenomenon allows part of the lances in a large elaborate picture to burn almost invisibly amongst the bright lights of other fireworks. When the reaction reaches the normal composition(s), the hidden lances blaze forth in a new design. Similar delay compositions can be made with other carbonates, barium nitrate, manganese dioxide, or even powdered wood ashes.

Current literature[139] suggests that traditional funnel and wire filling techniques and hand-rolled cases remain in use (Photo 15-12); a recent article[133] suggests a method of "inertial filling." The former method certainly produces an excellent product, but has not been in general use in the United States for many years, while the latter technique does not appear to have been adopted by any maker apart from its originators' now defunct manufacturing business. Domestic U.S. production of lances is done, typically one gross at a time, on air-actuated or drop-type gang ramming equipment. Spiral-wound tubes are used, typically 4⁵⁄₁₆" long and ⁵⁄₁₆" inside diameter, of approximately .015" wall thickness, with one end spun closed. The tubes are supported in a block of phenolic laminate material 4" thick, having 144 holes bored completely through, in a 12 × 12 array, so that only ⁵⁄₁₆" at the mouth of each tube protrudes from the block. A funnel plate of brass or aluminum fits over and supports the tubes' mouths. A shifting board of clay is loaded first, to form the bottom plugs of the lances; these are rammed, then the lance composition of choice is loaded and rammed in several increments until just short of the tubes' mouths. The block of tubes is removed from the press and the funnel plate replaced with a flat priming plate that fits flush with the ends of the tubes. A handful of lightly dampened lance prime (Formula 3, Table 15-4) is "buttered" into the tubes with a spatula, and the excess squeegeed from the top of the priming plate. The damp ends are sprinkled with meal powder to finish them, the priming plate removed, and the block is returned to the press in reversed position. With the rammers thus bearing against the closed bottom ends, the finished lances are pushed out of the block using their pressure.

The thoughtful manufacturer attempts, either through adjustment of the compositions, or by varying the amount of clay used to plug the bottoms of the tubes, to make the different colors of lances each burn for approximately the same length of time, so that all lances ignited at the same time finish burning as nearly

Table 15-3. Green and Yellow Lance Compositions.

	Green			Yellow		
	1	2	3	4	5	6
Barium nitrate	-	-	37	-	38.5	12.5
Barium chlorate	50	60	-	-	-	-
Potassium chlorate	35	-	-	70	38.5	-
Potassium perchlorate	-	30	10	-	-	50
Ammonium perchlorate	-	-	37	-	-	-
Sodium oxalate	-	-	-	22	-	25
Cryolite	-	-	-	-	11.5	-
Red gum	15	-	8	4	-	-
Shellac	-	-	-	-	11.5	12.5
Copal resin (KD gum)	-	10	-	-	-	-
Rosin	-	-	-	4	-	-
Hexamine	-	-	8	-	-	-

NOTES: Formula 2, found in the first and second editions of Lancaster[139] but suppressed in the third, is noteworthy for its use of KD gum, long considered an especially good fuel for green. Formula 3[133], with ammonium perchlorate, requires a special prime (Formula 4, Table 15-4) and is incompatible with the 'dead lance' composition because of potential formation of hygroscopic ammonium nitrate. Formula 6, containing sodium oxalate and barium nitrate, may prove hygroscopic in damp climates due to the possibility of formation of sodium nitrate.

simultaneously as possible. This uniformity is, at the least, an æsthetic desideratum, and, in the case of elaborate transformation pieces, necessary to their success. Nonetheless, such a concern is sometimes in conflict with other requirements, such as the prevention of "chimneying," the formation of an unwanted, clinker-like ash from the residue of the lance tube in conjuction with the dross from burning. Given the neglected state of set-piece work in present display practice, most manufacturers are forced to make compromises, and content themselves with turning out an economical and basically functional product, rather than an ideal one.

Although the theory of color emission has been discussed elsewhere, it is worth mentioning here the rationale for choosing particular color-producing chemicals. Metal chlorides usually give the best color spectra, but most of these salts attract too much moisture to be useful in commercial fireworks. Just as in military pyrotechny, chlorinated organic substances are commonly used to provide extra chlorine in the flame, although in many firework compositions the chlorate or perchlorate oxidizer itself is adequate for this purpose. When a chlorine donor is required, common choices are chlorinated rubber (called "Parlon," "Alloprene," "Super Chlon," etc.) chlorinated paraffin (Chlorowax), and powdered Saran resin, which is the same material used in plastic food wrap. Hexachlorobenzene is a very good chlorine donor and was formerly widely used in fireworks, but is less common today due to environmental concerns. Polyvinyl chloride, so common in military pyrotechny, is also used in display fireworks, but is not so useful in resin-fueled mixtures as in the high-temperature items containing aluminum or magnesium. Understandably, cost of ingredients is much more significant in devices intended for commercial sale than in military work. The fireworks industry is quite a small part of the overall chemical market, and it often has to make do with whatever is available. Manufacturers usually have to seek a balance between cost, availability, chemical stability, minimal water absorption and other factors.

Strontium nitrate is inexpensive and makes excellent red colors, but is hygroscopic enough that its practical use depends on the climate and the type of device being made. Red safety fusees invariably contain it, but they also have tight seals and a heavy wax coating which most fireworks lack. Strontium carbonate is inexpensive, non-hygroscopic and very widely used in fireworks. The oxalate has similar properties, but is much more costly and is not always commercially available. Strontium sulfate was once popular in plain red stars but now it is usually confined to specialized compositions. As a rule it is nothing more than the native mineral celestite ground to a powder. Because of varying impurities, the color produced is often inferior to that obtained from strontium carbonate, and today it also costs more than the carbonate. The chlorate and perchlorate of strontium produce excellent colors but are too hygroscopic for practical use.

Barium nitrate is cheap, non-hygroscopic and very stable, especially in mixtures that do not contain reactive metal powders. It is extensively used in green colors and many other effects, but usually requires a chlorine donor to produce a good green. Barium chlorate readily yields a deep green without the need for

Table 15-4. White and 'Dead' Lance Compositions and Lance Primes.

	White		Primes		'Dead'
	1	2	3	4	5
Potassium nitrate	64	-	71	-	-
Potassium perchlorate	-	66	-	58	-
Barium nitrate	-	13	-	-	-
Meal D	4	-	-	-	47
Sulfur	11	-	11	-	-
Charcoal	-	-	9	12	-
Antimony sulfide	21	-	-	-	-
Strontium carbonate	-	1	-	-	53
Red gum	-	20	-	6	-
Silicon, 325-mesh	-	-	-	12	-
Titanium, 325-mesh	-	-	-	12	-
Dextrin	-	-	9	-	-

NOTES: Formula 1 is a traditional saltpeter/antimony white lance; burning speed may be adjusted by varying the amount of meal powder. Formula 2, a perchlorate white lance, may require balancing of color by adjusting barium nitrate and strontium carbonate contents. Formula 3 is a prime for nitrate, chlorate, and potassium perchlorate lances; Formula 4[133] for ammonium perchlorate lances. Formula 5 is the 'dead lance' composition. It burns producing a glowing ash that is invisible at the distance of the audience. When the flame front reaches the color composition charged below the dead lance composition, this ignites and the ash breaks away, giving the appearance of color in mid-performance. The strontium carbonate acts solely as a diluent and heat sink. Burning rate may be changed by varying proportions of diluent and meal powder.

additional chlorine donors. Despite its sometimes fearsome reputation, it burns rather tranquilly with such fuels as shellac or gum copal, and quite high percentages can be used in torch or lance compositions when its cost is justified. Barium perchlorate is too hygroscopic for commercial use. Most other stable and affordable barium compounds, such as the sulfate, carbonate and oxalate, do not produce a good color except in high-temperature flames with magnesium. Barium carbonate is popular in small percentages as a stabilizer (acid-neutralizer) and as a modifier in glitter or tremalon (*q.v.*) mixtures.

Virtually all sodium compounds will color a flame yellow or amber; unfortunately most are hygroscopic. Sodium nitrate, so common in military flares with their sealed casings, is rarely seen in fireworks for this reason. Sodium bicarbonate is very inexpensive and easy to obtain, and it finds some use. Sodium oxalate is perhaps the most commonly used salt, but even this compound may cause problems under damp conditions, by reacting with oxidizers to produce sodium nitrate, chlorate or perchlorate. The native mineral cryolite (Na_3AlF_6) is among the few sodium compounds that are practically insoluble, and it does not attract moisture. It is available as a fine powder and is very useful in chlorate and perchlorate compositions, but is not so useful in black powder mixtures.

Blue and purple colors are considered more troublesome to produce than most others. Many preparations of copper have been employed, ranging from the metal itself in powder form to organic compounds like the benzoate, salicylate and octanoate. The best choice varies with the type of firework and the other ingredients in the mixture. Because copper hydroxide is a very weak base, many copper salts have a low pH and should be avoided in chlorate mixtures. Copper sulfate (blue vitriol) is one which has caused trouble in the past. Because it is inexpensive, always available, and not too hygroscopic, manufacturers sometimes succumbed to the temptation to use it in devices intended to be fired within a few weeks. Unfortunately, things do not always go as planned, and long-term storage of chlorate mixtures with strongly acidic salts like copper sulfate is very dangerous. In fact, devices containing this particular combination cannot be shipped under D.O.T. regulations – certainly one of the more welcome and sensible federal pronouncements about fireworks in the United States. The same concerns would apply to many other copper salts such as cupric chloride, bromide, and nitrate, but these are so hygroscopic as to be useless in the first place. Cuprous chloride is non-hygroscopic and quite safe to use, and with its chlorine content is theoretically an excellent choice[122]. In practice it is rarely used, because affordable, technical grade material is not a regular item of commerce. Traditionally, Paris green (copper acetoarsenite) was the most popular ingredient in blue star compositions; it burns well with minimal residue, can be used in high percentages, and produces a good color without chlorine donors. The sinister reputation of arsenic and the prevailing hysteria over toxins of all kinds have contributed to its abandonment, although some other common firework ingredients, such as the ubiquitous barium nitrate, are not exactly healthy articles of diet. Until about 1970, Paris green was used extensively as an insecticide, and to a lesser degree as a pigment; the firework industry represented only a small percentage of the total consumption. The virtual abandonment of Paris green in firework manufacture is largely due to the fact that it is no longer regularly used for *other* purposes. Few firework manufacturers have the time or inclination to make their own chemicals, and even white arsenic (As_2O_3), necessary as a precursor, is not as easy to obtain as it once was. Today, the most widely used copper compounds are the black (cupric) oxide, the basic carbonate, and the oxychloride. The last mentioned is not a discrete compound, but a hydrated mixture of chloride and oxide, and it varies considerably in color and density. When of good quality it gives admirable results in blue and purple stars, and is especially popular in chlorate mixtures. The carbonate is more often seen in perchlorate mixtures, and the oxide works well with either oxidizer but needs an especially good chlorine donor to produce a deep blue.

Waterfalls

Waterfalls are made with specialized torches which contain an excess of coarse metal powder. Long lines of these cases can be connected with quickmatch and suspended at a suitable height. According to Weingart[249], the gold Niagara falls composition containing saltpeter and iron filings was loaded in iron pipes of 1½" to 2" diameter, which could be cleaned with kerosene and reused almost indefinitely. This practice was obsolescent even at the time Weingart wrote. Today, most displays are not fired by the people who make the fireworks. Also, when waterfalls are made, they are usually silver ones based on aluminum flake with a chlorate or perchlorate oxidizer, and such mixtures would be dangerous in metal casings. Therefore cascade devices are now made with thin, consumable paper casings like ordinary flares.

Waterfall

Potassium chlorate	52
Potassium nitrate	9
Red gum	5
Aluminum, bright (*e.g.*, U.S. Aluminum #808)	17
Aluminum, flitters (*e.g.*, U.S. Aluminum #813)	17

The mixture is dampened with alcohol in the proportion of approximately 10% of its weight, and charged by funnel and rod into light paper cases ¾" to 1" in diameter, 8" to 12" long. Instead of handles, the butt ends are equipped with soft iron wire which makes it easy to attach them to a rope, the underside of a bridge, or other support. As noted by Lancaster[139], many people are inclined to use barium nitrate mixtures for safety reasons, but "there is a tendency to get a large glare at the mouth of the tube and a weaker drop effect." More detail on making waterfalls can be found in an article in PYROTECHNICA • XII[232].

Sparklers

Sparklers have much in common with torches, although they have no casings. While they appear to be very simple devices, making them can involve many complications reminiscent of those in match manufacture (see Chapter 11). The viscosity of the slurry and the temperature and humidity of the drying area have significant impact on the finished product. The amount of composition on a sparkler is much greater than that on a household match, and it must be applied evenly over a length of several inches and dried without cracks or excessive lumpiness. Furthermore, sparklers are among the few consumer fireworks that are regularly used indoors, so they should not produce molten dross and the sparks should not persist long enough to constitute a fire hazard. The glowing wire core is the principal hazard, and sometimes comes under attack from consumer protection groups. However, attempts to replace the wire with other materials have not been very successful, because its heat-conducting properties are important in keeping such a small column of pyrotechnic material burning regularly. Like all devices which produce fire, sparklers can be dangerous if handled carelessly, but considering the numbers sold, the proportion of accidents is not very high. In the United States, regulations permit sparklers to be retailed having up to 100 grams of composition, but the amount drops to only 5 grams if chlorates or perchlorates are used. A typical sparkler composition uses barium nitrate as the oxidizer, with fine flake aluminum powder, steel filings, a dextrin or gum binder and various minor additives.

Sparkler

Barium nitrate	44	51
Aluminum	25	6
Iron powder (treated with paraffin)	19	34
Potassium nitrate	4	–
Charcoal	–	0.5
White dextrin	8	8.5

Sparkler mixture is dampened with 30-35% of its weight of cold water, and mixed to a smooth and uniform slurry into which the wires are dipped. Normally they are dipped twice, drying in a current of warm air between dippings. White dextrin is the preferred binder for sparklers. Its lower solubility (as compared to the more usual yellow dextrin specified for stars) presents no problems when the water content is as great as it is in such a slurry, while the greater viscosity that results from its use is of positive benefit in keeping the other ingredients in suspension.

Senko hanabi are sometimes described as Japanese sparklers, though the resemblence to the Western product is slight. The effect depends upon a rapid initial combustion of a mixture of potassium nitrate, sulfur, and pine soot, forming a molten droplet of semi-combusted reactants from which lacy "spur-fire" sparks are thrown, the whole effect lasting less than one minute. Two types are made, one a dipped stick (hence the comparison to sparklers), the other consisting of dry composition twisted up in paper. Maeda[155] reports the first composition, Shimizu[139] the second:

Senko hanabi

Potassium nitrate	54 – 58	61
Sulfur	23 – 26	24
Carbon (pine soot)	23 – 16	15

Also sometimes characterized as a sparkler is the *morning glory*, really a small color-changing torch, about the size of a lance, attached to a wooden stick with twisted decorative tissue paper.

Gerbs and Fountains

When a strong casing is charged with a relatively fast-burning composition, considerable pressure may be generated as the mixture burns. Obviously if this pressure is excessive, the casing will burst, but when these factors are in proper balance it is possible to produce a controlled jet of flame or sparks. In most devices of this type, the burning rate is moderated by compacting the powder into a solid mass; pyrotechnic compositions burn more slowly and predictably when loaded in this manner, although most of them soon reach a point where further compression has no appreciable effect on burning rate. There is usually some gain in performance as well, since increased loading density allows more composition to be burned in a given space. These general principles of ramming or pressing composition in tubes are the same for many types of fireworks, ranging from fountains to serpents, hummers, wheel drivers and skyrockets. Usually the open end of the tube is constricted for a further increase in pressure and combustion efficiency. The reduced-diameter orifice is sometimes called a "nozzle," a term adopted from rocketry; a better established term is "choke." When firework factories rolled most of their own tubes, choking could be done while the tubes were still damp with paste. Each tube was placed on a metal nipple of the appropriate size and constricted with a loop of strong twine resembling a garotte, or by a mechanism resembling the iris diaphragm of a camera lens. With high-quality paper, such pulled-in chokes worked very well; indeed they are superior for some compositions. Today, when most tubes are purchased from specialist suppliers, it is not practical to choke them in this manner, and in most cases a clay choke works just as well. Clay is usually rammed as a dry powder, although it may be slightly moistened with kerosene or other liquids.

Rammers are normally simple rods of aluminum, brass, or bronze – occasionally hardwood or synthetic materials – which fit smoothly inside the tubes. Hydraulic pressing is preferred for loading many tubes at one time, for sensitive mixtures, and for very large single devices. However, hand ramming is still widely practiced, using mallets of non-sparking materials such as rawhide, lignum vitæ, or lead. Such loading techniques involve a great deal of experience and "feel," and it is not possible to give detailed guidelines here. In general, larger mallets are used for larger items, and most tubes are rammed about as firmly as possible to do without bulging or splitting them, or making cracks in the composition, which usually cause an explosion when the device is fired. Sometimes, tubes are rammed in a "mould" which fits them snugly on the outside and allows them to withstand greater loading pressure, but this time-consuming technique, with the need for high precision of case and mould dimensions, is not used as often as it once was.

In some cases, a choke is made by ramming clay solid (as for an end plug) and then drilling it with the proper size bit. More commonly, the empty casing is placed on a short metal nipple and the clay is compacted around the nipple. A rammer drilled with a longitudinal hole, called a drift, accommodates the tip of the nipple and prevents it from being damaged. After the choke is formed, the device can be filled with rammed increments of composition. Sometimes the mixture is dampened with a small amount of water, alcohol or other liquid to reduce dust; more commonly it is loaded as dry powder. Typically each charge of composition makes a compressed layer about the same height as its diameter, although smaller increments may be chosen where very hard and even compaction is important. With a given mixture it is important to use the same size increments together with the same pressure setting, or when hand ramming, the same number of blows from the mallet. Often, two or more compositions are loaded sequentially in the same tube, and when the transition is made, the ramming pressure may change as well. After the final increment has been rammed, a charge of commercial grain powder may be added for a type of report traditionally called a "bounce." This practice is not suited to gerbs which may form a part of large set pieces, and today it is usually frowned upon in consumer items. With or without a "bounce" it is important to have a strong plug at the end of the gerb or fountain, usually consisting of solidly rammed clay.

Perchlorate and even chlorate mixtures can be used successfully in choked tubes, but if this is done, the balance between burning rate and choke constriction becomes more delicate. Cracking or loosening of the charge due to rough handling can easily turn such devices into unintentional but powerful firecrackers. Furthermore, chlorate and perchlorate mixtures are more hazardous to ram. Therefore practically all commercial fountains are made with nitrate oxidizers (Table 15-5). The *gerb* or *gerbe* consists of a black powder based composition rammed in a choked casing as described above. This old name, from the French word for a sheaf of wheat, is never seen on American consumer fireworks but is still common in professional display work. Sizes vary, but a typical gerb is about 3/4" i.d. and six to ten inches long. Traditionally, the spark-producing ingredient was either steel filings or an excess of coarse charcoal. Steel and iron have the unfortunate property of rusting when in contact with potassium nitrate, and, for use in fireworks, are coated with paraffin wax, or a drying oil such as tung or boiled linseed, to prevent this. Since the particles of these metals used in fireworks are typically by-products of some machining operation such as turning or boring, they are usually mixed with lubricant "cutting oil" used in those processes. This must be removed by washing with a de-greasing solvent prior to coating, as otherwise it can interfere with successful adhesion of the wax or drying oil. Another very old style of gerb produces a smaller but very concentrated jet of white or gold flame. These are not very entertaining when fired singly, but are useful in set pieces to make star or sunburst designs, or, when fired at right angles

Table 15-5. Gerb and Fountain Compositions.

	1	2	3	4	5	6	7
Potassium nitrate	52	52	31	53	17	52	-
Charcoal, air float	13	13	6	-	-	10	-
Charcoal, 36-mesh	-	-	17	16	-	-	-
Sulfur	9	9	4	10	11	7	-
Meal D	-	-	42	-	-	-	67
Antimony sulfide	-	-	-	-	-	14	17
Sodium oxalate	-	-	-	-	-	-	7
Barium nitrate	-	-	-	-	35	-	-
Barium carbonate	-	-	-	-	-	10	-
Aluminum, dark (U.S. Aluminum #809)	-	-	-	-	17	-	-
Aluminum, bright (U.S. Aluminum #808)	-	-	-	-	9	-	7
Aluminum, flitters (U.S. Aluminum #813)	-	-	-	-	11	-	2
Aluminum, atomized (Reynolds #120)	-	-	-	-	-	7	-
Steel filings, treated 20-40 mesh	26	-	-	-	-	-	-
Calcium silicide, 20-40 mesh	-	-	-	16	-	-	-
Titanium, 20-40 mesh	-	26	-	-	-	-	-
Dextrin	-	-	-	5	-	-	-

NOTES: Formula 1 is a steel gerb; Formula 2, a titanium gerb, is similarly formulated. Formula 3 is a charcoal gerb using coarse charcoal to produce reddish-gold sparks. Formula 4 is an unusual composition for a cone fountain. The first increment of composition is lightly dampened and pressed into the tip of the cone to plug it. The remaining composition is scooped in dry, and the cone closed with a heavy chipboard disc cemented into place. The effect is a white spark spray. Saltpeter, charcoal, and calcium silicide must all be coarse for the cones to succeed. Formula 5 is a silver gerb for unchoked 3/4" cases 6" long. The composition is dampened with about 10% of its weight of alcohol and charged by rod and funnel. Case walls must be thick to avoid burning through. Formula 6, a white flitter, and Formula 7, a gold flitter fountain, are for 3/4" to 1" choked cases 7" to 9" long. The choke aperture should be one-third to one-half the case diameter.

Table 15-5. Gerb and Fountain Compositions (continued).

	8	9	10	11	12
Potassium nitrate	55	52.5	64.7	52.0	47.1
Sulfur	20	20.0	23.5	23.7	28.4
Lampblack	20	22.5	8.8	9.5	9.8
Antimony sulfide	5	5.0	-	-	4.9
Arsenic trisulfide	-	-	3.0	7.4	-
Meal D	-	-	-	7.4	9.8

NOTES: Formulæ 8 – 11 (Rev'd. Ronald Lancaster, private communication) and 12[30] are traditional 'flowerpot' fountains, best appreciated at close proximity. The range of proportions of the ingredients illustrates the adjustment that must be made to case dimensions and the properties of available varieties of lampblack.

to each other, a very attractive mosaic pattern. Within the past century other modifications of the black powder gerb have become popular, notably sparkling or glittering effects made with aluminum. Titanium has become available at a reasonable price as a by-product of the aircraft industry, and is an easy way to produce bright silver effects. It has the advantage, like aluminum, of not requiring treatment.

"Fountain" is a very general term applied to any tubular firework which does not move, but merely produces a spray of sparks. All gerbs may be considered fountains, but not all fountains are gerbs. One traditional type which is not called a gerb, although it is loaded in the same way, is the "flower pot" (Table 15-5, Formulæ 8-12). Its distinguishing feature is a small percentage of lampblack combined with a lot of saltpeter and sulfur, and often a sulfide of arsenic or antimony. Historically, the usual choice was orpiment, As_2S_3. This composition produces a great quantity of molten droplets. When expelled into the air, these droplets glow dull red at first, then burst into the bright gold "flowers." Flower pot compositions burn more slowly than most gerb mixtures and are less likely to burst their casings; also the sparks burn cooler and are less dangerous than those produced by iron or other metals. Traditionally, these fireworks are fitted with wooden handles so they can be held while burning; they are still sold in some countries. It is worth noting that the term "flower pot" is also applied to fireworks in a completely different way, to describe a star shell which explodes prematurely in its mortar and sprays its content skyward in a bouquet pattern.

Some fountains do not have chokes at all, and in this case, tubes may be thinner and compositions need not be consolidated so firmly. A funnel and rod technique is convenient for filling large numbers of small-diameter tubes. Larger fountains are often made with little or no choke when the powder charge includes granules or cubes of a different composition, designed to produce points of colored light against a contrasting background of sparks. This is an old practice which declined in popularity due to difficulty in adjusting the performance, as well as fear of ramming chlorate granules in matrices containing sulfur. Today, the idea has been revived, but usually with "microstars" containing magnalium alloy and nitrate oxidizers. The Chinese are especially adept at making such fountains, which have captured a large part of the consumer fireworks market.

Mixtures containing barium nitrate and high percentages of flake aluminum are relatively inexpensive and produce bright silver sparks, but they burn at very high temperatures and demand careful selection of casings. Such mixtures can be hazardous as loose powder but once rammed, they are quite safe; indeed they are very hard to ignite and require special priming mixtures if they are to be used with the common visco fuse. Often they are used as secondary effects which follow a more traditional and easily ignited black powder composition.

Conical fountains are very popular as consumer fireworks. At times they have earned a reputation as overpriced "ripoff" items when a large, gaudy cone contains only a small charge of composition at its tip. Such practices are only encouraged by government regulations which strictly limit the amount of powder in each cone. When well made, cones have much to recommend them as back yard fireworks. Their wide bases allow them to stand solidly without being driven into the earth as is necessary with tubular fountains. The small tip functions as a useful choke, and the shape of the charge ensures that the effect increases as burning proceeds. This shape also permits cones to begin with a small amount of colored fire, which would be ineffective and possibly explosive in a choked tube. Cones are especially effective with traditional mixtures of iron filings and black powder ingredients. The shape makes hard ramming impractical, so the compositions are simply packed in gently with a hand tool. This is one application where compositions may be dampened with alcohol, whether or not they contain a resinous binder. The end plug is usually a simple cardboard disc, glued in place.

Wheels and Related Devices

Wheel drivers bear a very close resemblance to gerbs; indeed they are often loaded with the same set of tools, and they use quite similar compositions of the black powder class. With drivers, the need for propulsive force and regular burning outweighs any desire for maximum spark output, so driver compositions (Formulæ 1-3, Table 15-6) usually contain lower proportions of metal powders. Often they have high percentages of commercial gunpowder, either meal powder or fine grain such as 5FA or 7FA. Technically, a wheel driver is nothing more than a type of rocket engine – and the same can be said of serpents and many other items – but these devices are never called rockets in the world of fireworks. Compared with skyrockets of the same size, drivers have lower thrust and usually much longer burning times. In loading drivers, the final increment of composition is usually not plugged, which makes for positive fire transfer to the next device(s) in the series. Both ends are typically given paper nosings, which makes it easy to tie in quickmatch. Sometimes drivers made to be the final ones in a series are equipped with reports or simply plugs of clay; then of course, no nosing is used.

Drivers vary from ⅜" bore in small consumer wheels, up to 1¼" or 1½" bore. It is rare to see them any larger because cases of this size become difficult to ram properly by hand, and most firework makers do not wish to invest in tooling for very large sizes which would be used only rarely. Thus, even the largest exhibition wheels, instead of using 2" diameter drivers, are likely to have clusters of smaller ones. Common sizes are ½",⅝", ¾", and 1" bore. A four-foot wheel fitted with half a dozen ¾" cases might be matched so they will burn in pairs, in trios, or all six at once, depending on the strength of the drivers and the effect desired.

Pinwheels are made from long, small diameter tubes which are flexible enough to be rolled up in a spiral shape. Since they are unchoked, they require very fast-burning mixtures – usually with a high percentage of grain powder – in order to produce enough thrust to make them spin. The compositions are not rammed solid; instead the little pipes are merely poured full and are softened in damp cloths until they can be bent. Once rolled, they are attached to cardboard discs and allowed to dry. Usually the backing discs have reinforced holes in the centers,

Table 15-6. Wheel Driver (Pusher) and Pot (Case Color) Compositions.

	Drivers			Pots		
	1	2	3	4	5	6
Extra-fine meal	-	90	68	-	-	-
Meal D	50	-	-	-	-	-
Potassium nitrate	33	-	17.5	-	-	-
Charcoal, air float	10	-	3.5	-	-	-
Sulfur	7	-	2	-	-	-
Titanium, 30 mesh	-	-	9	-	-	-
Steel, treated, 30 mesh	-	10	-	-	-	-
Potassium chlorate	-	-	-	46	11	56
Potassium perchlorate	-	-	-	23	-	-
Barium chlorate	-	-	-	-	31	-
Barium nitrate	-	-	-	-	21	-
Strontium carbonate	-	-	-	14	-	-
Sodium oxalate	-	-	-	-	-	5
Aluminum, bright (U.S. Aluminum #808)	-	-	-	-	21	23
Aluminum, flitter (U.S. Aluminum #813)	-	-	-	-	11	11
Red gum	-	-	-	-	5	5
Shellac	-	-	-	17	-	-

NOTES: Formula 1 (charcoal), Formula 2 (steel), and Formula 3 (titanium), are all rather energetic compositions intended for small ½" drivers or 'pushers' of the sort used on a typical display wheels 24" to 36". Formulæ 4-6 are for pots; Formula 4 is red, Formula 5, green electric, and Formula 6, yellow electric.

which allow the pinwheels to be nailed to a fencepost or other upright object. They can also be fitted with a small point or protuberance which allows them to spin like tops on a paved road or other flat surface. Very small ones, about 1¼ inches in diameter, are made by the Chinese and are sold under the name "Camellia Flowers."

Saxons are another type of small rotating device, with a very long history. Both ends of these fireworks are plugged with clay, and their vents or "chokes" are simple holes which are bored through the *sides* of the casings near the ends. A saxon spins rapidly around its central axis. Some saxons, especially large ones, have been made in two pieces and joined to a central wooden boss. Normally a single tube is used; clay is rammed in the central portion, which is later drilled to accommodate a large nail. Both ends can be matched to burn simultaneously, but this is uncommon. As a rule, the first side to burn is drilled with a second hole, next to the central clay barrier, and this is connected to the vent on the far side. If all three holes are on the same side of the tube, the saxon will reverse direction when the second half ignites. This is an eye-catching manœuvre which throws a shower of sparks, and is especially lively in small saxons with low rotating mass. Many traditional saxon compositions are very plain, hot-burning ones containing only gunpowder, saltpeter and sulfur. However, they work well with showier mixtures containing excess charcoal or metal powders. Saxons are not very common as consumer items in the United States, and when they are seen at all it will be under some trade name instead of the generic term. However, they remain fairly common in display work, sometimes called "merry-go-rounds." Class B saxons may be ½" to ¾" i.d. and ten to twelve inches long, with quickmatch fuses.

With all the foregoing devices in mind, a little imagination will suggest designs for large and elaborate ground displays or "set pieces," containing both fixed and moving elements. Lancework pictures can be enhanced with a wide variety of other fireworks. Gerbs may be arranged to produce checkerboards of fire, with saxons or pinwheels spinning away inside the squares. Wheels are subject to almost endless complications, ranging from simple lances or color pots attached to their spokes, to very large wheels which carry many smaller ones. The color pots with which vertical wheels are ornamented are basically large lances, or short torches, ¾" to 1" in diameter, and 3" to 6" long; the length varies according to the burning rate of the composition. The cases are formed of a few thicknesses of kraft paper, or they may be thin-walled spiral-wound tubes. The ends are plugged with clay or sawdust, and affixed with glue and a double-pointed nail to the spokes of the wheel in the same way that lances are attached to their frameworks, taking especial care that the pots are firmly secured and do not fly off the wheel as it is spinning. Many compositions may be used for the purpose; the composition given for waterfalls makes a good pot, as do those for some of the illuminating colored stars and strobe stars. Formulæ 4-6, Table 15-6, are specifically adapted as "case colors" for wheel pots.

Horizontal wheels are less common than vertical ones, but can be equipped with waterfall cases, or they may even fire volleys of small ærial fireworks from their rotating frames. Large fancy wheels and related ground fireworks are

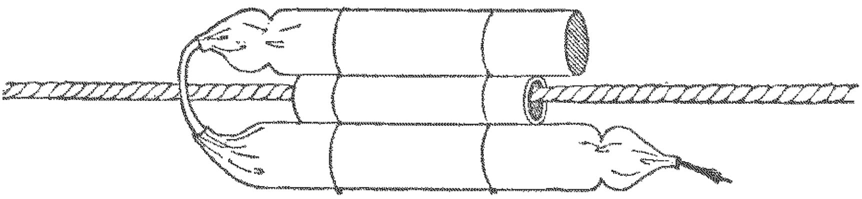

Figure 15-2. Line rocket.

practically curiosities in the United States and many European countries; they were more common 250 years ago. Many authors have blamed their demise on the profusion of deeply colored stars, whistles and other ærial effects which were perfected in the nineteenth century. However, most of these components can also be used in ground pieces if desired, so to some degree, the issue must be considered one of changing fashion or cultural tastes. In some countries such as Mexico and Malta, elaborate ground displays with large wheels still play a central rôle in firework shows.

Line rockets (Fig. 15-2) are usually made by attaching wheel drivers to an empty tube which slides along a taut cord or wire. Usually the devices are made so as to change direction several times, and they may have drivers which make them spin as well. A traditional use is to carry fire from one set piece to another in a visible and dramatic fashion. Line rockets are also called "flying pigeons" or occasionally "rats." Like other ambitious ground fireworks, they are rarely seen in English-speaking countries.

In addition to wheels which rotate around fixed axes, various free-spinning devices are popular as consumer fireworks. Typically, these resemble one-half of a saxon, with a single jet hole near one of the clay end plugs. They begin with a fast black powder mixture, but in most of them, the main effect is due to a metal-fueled composition. The Chinese have dominated the market for these items, using magnalium compositions which produce good red, green and yellow colors and which exhibit large flames despite having to pass through the small vent holes. Successful fireworks of this type are usually small, with outside diameters of 1/4" to 3/4" and lengths of 1 1/4" to 3". The high-energy compositions make them spin very rapidly with a buzzing or whining noise. Depending on the mixture and the angle of the jet, some of these fireworks can fly under their own power and are more properly classified as ærial devices. The ground types are usually longer in relation to their diameter, and they move with a combination spinning and tumbling motion, producing a flame pattern with a floral appearance. One of the best known of these products is the "Ground Bloom Flower," which changes colors and burns about ten seconds, a long time for such an energetic device. The smallest of these spinners resemble Chinese firecrackers, and in fact are braided into flat packages in the same way. "Jumping Jacks" are representative examples.

Serpents, squibs, or *chasers* are self-propelled tubes which resemble small wheel drivers. As with many firework terms, these words are often used in a rather arbitrary manner and are practically interchangeable. "Serpent" is perhaps the most common name, and is applied to small choked cases rammed with strong gunpowder mixtures, whether they are fired singly on the ground or loaded into ærial fireworks.* Compositions are similar to those used for small wheel drivers. The word "squib" is now commonly applied to ignition devices used in pyrotechny, especially electrical ones. However, the classical squib was a small serpent, about 1/4 inch in diameter, with a black powder report. Part of the fun in using squibs was to run after them and step on them; they were not powerful enough to cause injury through a leather shoe sole, and the additional confinement made a louder bang. *Saucisson* is a term not commonly heard today, but was applied to relatively short, thick serpents with reports, used as garnitures in rockets, shells and mines. True saucissons had pulled-in chokes, and when the report end was also crimped shut and tied with string, they had the appearance of small sausages (it is amusing to note that in Britain some types of sausages are called "bangers;" thus while the French named a firework after a sausage, the English apparently named a sausage after a firework). The term "chasers" is a relatively recent one, applied to serpents which are sold to the public and are meant to be fired on the ground. In the 1940s they were deemed "nigger chasers,"[249] and the accepted targets have varied with the political climate of the times; for example in the 1980s, similar devices were sold as "Iranian chasers." Chasers usually end with a flash report, and today, whistling ones are more popular than the gold sparkling type.

Whistles

The whistling effect is a very common one, and has become almost inseparable from fireworks in the popular mind. Indeed, in television and motion pictures the sound is likely to be heard with types of fireworks which do not usually whistle, and in scenes set in periods before this effect was developed! Many a curious youngster has dissected a whistling firework, expecting to find some kind of angled orifice like that in a dog whistle or an elk call, only to be all the more perplexed on finding a simple, open-ended tube. In the eighteenth century and earlier, metal tubes resembling flutes were occasionally attached to large skyrockets, where the airflow was fast enough to make them whistle. However, the whistling fireworks in use today depend on specialized compositions which burn in a rapidly pulsating fashion. This phenomenon is explored in Chapter 21, and the compositions provided in Table 21-2 are also representative of those used in recreational fireworks over the years.

The first published description of pyrotechnic whistles is that of Amédée Denisse in 1888[45]; one British authority[26] says they were first used at the Crystal Palace displays in London but does not give a specific date. In any case, it seems safe to say that they are a development of the mid-Victorian period, and were very popular by the beginning of the twentieth century. The original compositions were based on potassium picrate with an additive, usually potassium nitrate, to control the burning rate and reduce the likelihood of explosion. Picrate

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* Their curved and erratic motion suggests the movement of snakes.

Table 15-7. Whistle Compositions.

	1	2	3
Potassium perchlorate	-	75.2	66
Potassium chlorate	76	-	-
Sodium benzoate	20	-	-
Sodium salicylate	-	19.8	28
Petrolatum	3	-	-
Paraffin oil	-	3	-
Red iron oxide	1	2	-
Titanium, 20-40 mesh flake	-	-	6

NOTES: Formulæ 1 and 2 are due to Öztap[181]. The paraffin (mineral) oil or petrolatum are mixed with toluene or other suitable solvents, and the solution is then added to the salicylate or benzoate in a mixer to form an emulsion. Finally, the oxidizer is mixed with the emulsified ingredients by kneading, granulated through a screen, then dried.

whistles are still made in some countries; they are admired for their clean shrill sound, and their black smoke trails give them an added dimension for daytime use. Even so reliable an author as Tenney L. Davis[44] has stated that picrate whistles, and colored stars made with picric acid, are too shock-sensitive to be used in shells – something which is not really true. Some of the old Italo-American firms for many years used enormous numbers of picrate whistles as shell garnitures. However, today picric acid and its salts have a reputation for being very hazardous and are rarely found in any kind of commercial product in the United States. Many people assume that an unacceptable level of danger forced the change in whistle manufacture. The truth is that all whistle compositions are quite sensitive to shock and friction, and must be handled with great care. The potassium chlorate/gallic acid mixture, the earliest "safe" alternative, is actually more sensitive to friction than potassium picrate. In loose powder form, whistle compositions are almost as explosive as flash powder; in fact, the original whistling chasers did not use a separate mixture for the report but simply had their last increment of powder loaded loosely, instead of compacted. The use of picric acid does have many drawbacks. The picrates of heavy metals *are* truly dangerous primary explosives, comparable to the materials found in blasting caps, and for this reason picric acid should not come in contact with the brass sieves, lead ramming blocks and similar tools so common in firework factories. Iron and steel are to be avoided because of the spark hazard, so a dedicated set of aluminum tools – which wear out faster than brass or bronze – is about the only practical option for working with picrates. Because of the decline in its use for other purposes, a technical grade of picric acid is usually not available, and the laboratory or reagent grade costs around $30 per pound. Picric acid and soluble picrates are powerful yellow dyes which are messy to handle. Finally, the name is aptly derived from the Greek (πϊκρία), meaning bitterness, and even a small amount of dust in the air tastes like a dose of quinine. As Lancaster[139] says, "Picric whistles are not popular with firework makers mainly because no one cares to work with them."

Fortunately, many different aromatic compounds – that is, those having structures which include the benzene ring – will burn in a suitably oscillatory manner when combined with a chlorate or perchlorate oxidizer. As usual, cost and availability are of paramount importance for commercial work. Gallic acid is still in use, and phthalate salts are reportedly used by the Chinese, but today the most common whistle fuels are sodium salicylate, and the benzoates of sodium and potassium. The potassium perchlorate/benzoate version is probably as safe as any composition in this class. Sometimes catalysts, such as iron oxide or other transition metal compounds, are added to these whistle compositions in order to alter the pitch or increase performance; usually the catalysts increase sensitivity as well. Formulæ 1 and 2, Table 15-7, illustrate the use of iron oxide as a catalyst. They also contain either paraffin oil or petrolatum (vaseline) to help lubricate the mixtures, lowering the danger from friction in mixing and filling, and protecting to some degree against uptake of moisture. Their use has an additional benefit beyond safety, facilitating granulation, and so making the mixtures free-flowing in shifting-boards used for loading.

Whistle tubes are not pressed completely full; an empty space about an inch long is customary at the open end to produce the sound. The sound will vary somewhat with the length and diameter of the tube, but only a limited amount of "tuning" is possible since each composition has its own preferred frequency range. Larger diameter tubes produce louder noises, but a point of diminishing returns is quickly reached so that, for example, a one-inch diameter whistle may be only slightly louder than a half-inch, even though it burns four times as much composition per second. Large whistles are more likely to explode and are much more destructive when they do so. Therefore, whistling components, both in consumer and in display fireworks, rarely exceed ½-inch inside diameter. Whistles may be combined with practically any other type of firework, and are especially popular in fountains, wheels, and ærial shells. Recently it has become a common practice to add titanium to whistles, producing a silver tail without much change in the sound (Formula 3, Table 15-7). Titanium does not cause a significant increase in the sensitivity of finished benzoate or salicylate whistles, although it is especially important to be careful about friction when charging loose powders containing this metal.

Benzoate and salicylate whistle compositions are characterized by low cost, high energy output, and (except when they contain metal powders) low light output. These properties have made them increasingly popular as propellants in some tube items and as bursting charges in ærial shells. Such uses are especially popular among hobbyists, and have also been adopted by some American manufacturers. Needless to say, such techniques would not be recorded on a product label, but it is worth mentioning that if one hears a pyrotechnist speak of a "whistle break" in a shell, this does not always mean the shell contains whistles. Instead it may refer to the bursting charge itself.

Smoke

Smoke is covered extensively in Chapter 20, and as with whistles, most of what has been said about military pyrotechnics applies to the recreational kind as well. Except for white smoke, practically all the colors used in consumer fireworks are made by the sublimation of powdered dyes. Many of the dyes recommended in older literature are practically impossible to obtain now; the usual choices depend less on theoretical ideals than on which dyes are available in the chemical market at a given time.

Colored smokes generated by chemical reactions are hardly ever seen in the small fireworks sold to the public. At one time, yellow smoke was commonly made with realgar and orpiment; these sulfides of arsenic are practically insoluble and are not very toxic if ingested in small amounts. Nonetheless, all arsenic compounds have been barred from consumer fireworks in the United States. Furthermore, the arsenic sulfides, which were once no more expensive than that of antimony, are now very costly and difficult to obtain, which has limited their use in fireworks of all kinds. In some countries, notably Japan, they are still employed in special daylight fireworks, as are black smokes made from naphthalene or anthracene, very similar to the military types.

Explosive Noisemakers

Explosive fireworks are found in all countries where fireworks are made, and they exist in great variety. Indeed, the desire to create explosions seems to be an integral part of many cultures, and is perhaps older than gunpowder itself. The Chinese had a tradition of throwing green joints of bamboo into bonfires, where steam pressure causes them to burst with loud bangs. The word "firecracker" is often ignorantly used as a generic term for fireworks of other kinds, which if nothing else, reflects the near univeral appeal of firecrackers. Today it is safe to say that these explosives are popular with almost everyone except politicians and bureaucrats. In modern industrialized nations, there has been a tendency to treat the devices, rightly or wrongly, as an unwarranted threat to public safety. Even some people in the fireworks business have a distaste for firecrackers and the misuse which seems to accompany them, and there have been some types the manufacture of which was voluntarily suspended. More commonly they are subject to convoluted and often ineffective laws. Some countries, such as Canada, completely ban flash crackers, but are relatively lenient about black powder types. The United States imposes a minuscule 50 mg powder limit regardless of composition, and some individual states do not even permit these small crackers. Germany, which has long had a reputation for repressive and humorless government, permits vastly larger firecrackers than the "Land of the Free." Roman Catholic countries such as Spain, Portugal and Malta, where fireworks are intimately associated with church feast-days, are generally quite liberal on the subject of exploding fireworks.

Black gunpowder has somehow acquired a frightful reputation in the media, but in normal quantities it requires a strong container to produce an explosion. In the days when it was the only explosive on the market, making loud reports without resorting to metal casings was quite a laborious process. Noisemakers of this kind were often called "maroons," after the French for chestnuts (*marrons*), which often burst while being roasted. All the classic works on pyrotechny describe maroons made from small cardboard boxes or cylinders, which were wound with multiple layers of strong twine and then dipped in glue for additional strength. For countless centuries, the Chinese have made firecrackers from small tubes of coarse brown paper, with colorful wrappers and tissue paper fuses. They are able to produce enormous quantities with very simple tools; for a detailed account of the procedure the reader is referred to Weingart[249] and Davis[44]. The traditional black powder version, often known as Mandarin crackers in the higher grades, were imported into the United States well into the twentieth century. They varied greatly in potency, one of the main reasons being the difficulty of getting the powder confined well enough. Most crackers of this type had clay at each end, and the paper was also turned in to produce a sort of crimp. The highest quality ones had the ends bound tightly with thread to provide a stronger closure. Even the best Mandarin crackers were not as loud as similar-sized flash crackers, and today there is little demand for black powder crackers except where other types are forbidden.

One very old and cleverly designed black powder device is the English cracker or "grasshopper." To make these, long narrow paper tubes are filled with fine grain powder and are dampened slightly as described previously for pinwheels. Instead of being rolled into spirals, cracker pipes are folded back and forth to form 180-degree bends. They are tied at each bend, as well as over their whole length, and are allowed to dry. The powder burns smoothly in the straight sections, but the sharp corners provide enough confinement to produce small explosions. The frequency depends on the quality of the powder and the diameter of the column, but the intervals between bangs are quite regular in well-made examples. Besides being fired on the ground, English crackers were once extensively used as garnitures in rockets, mines and shells, and when old texts refer simply to "crackers" it is these devices which are intended. Today they are less common but are still available to the public; one Chinese brand is designated "Jumping Frogs," which is an apt description of their movements.

The widespread adoption of chlorates in the nineteenth century had a profound influence on the manufacture of fireworks, including the exploding ones. Chlorate mixtures are much more powerful than black powder and no more costly; indeed most of them are less expensive than good grain powder. For a while, the old-fashioned cubical maroons were made with chlorates, but the most famous (or infamous) of the chlorate noisemakers was the American cannon cracker, which was also one of the first fireworks to be made in large quantities by machine. Some of the largest Chinese black powder types were also called "cannon crackers," but the American version soon dominated the market. They had relatively thick parallel-wound casings, with end plugs of various materials including clay and cork. Typical fuels were sulfur, antimony sulfide and charcoal dust, and sometimes powdered resins or metallic antimony, all of which make very powerful mixtures with the chlorate oxidizer. These compositions are rather dense and have a tendency to pack or cake, which – as with powders which are intentionally compressed – slows the combustion and weakens the explosion. To help prevent this problem, cannon crackers were filled only about half full. One well-known work on homemade explosives claims that the ideal is one-third full, but much depends on the individual composition. There was undoubtedly an element of merchandising psychology involved, with a desire to make the product look as large as possible for a given price. Even if only a third full, cannon crackers made an impact, in more than one way. Old cartoons depicting firecrackers which resemble sticks of dynamite may seem to be examples of artistic license, but they reflected reality. *Small* cannon crackers were two or three inches long, and some of them reached lengths of a foot or more. Aside from the tremendous power, the relatively thick casings and hard end plugs sometimes created flying debris, and the types of fuse employed also contributed to the potential hazards. Some of the early crackers were fused with bare match, which is too fast for such potent explosives. Blasting or dynamite fuse was much slower and more regular, but its flame progression could not be observed, which sometimes caused inexperienced users to think the fuse had gone out. Cannon crackers were fading from the scene even before World War II, due partly to restrictive laws and partly to the popularity of flash crackers. Few people other than pyrotechnists and very old men could now give an accurate description of a cannon cracker, but even today, some of the attitudes toward exploding fireworks which are seen in the media and the legal system appear to be a legacy of the cannon cracker era.

Magnesium flash powders were used in photography from the 1860s on, and the explosive character of the faster kinds quickly became known. Photographers tended to use the slowest type that would work for any given job, and the use of the "hottest" ones, especially indoors, was a task for experts. Improper use could not only injure or deafen people, but is known to have blown the windows out of buildings! Except for exhibition-grade ærial displays, magnesium was not normally used in fireworks, due to its high cost and poor storage properties. When aluminum powders became affordable in the 1890s, firework makers began to experiment with them. Most were silvery flake powders with stearin coatings, originally designed for use in paint. Soon very fine, reactive flake powders called "pyro-aluminum" were being specifically made for the firework industry. Some of these have particles so fine that they no longer appear silver, and are called "dark" or (with some exaggeration) "black" aluminum. Chlorate/aluminum flash powders, and most perchlorate ones, have the mixed blessing of requiring very little confinement to produce an explosion. This property makes them dangerous to mix and store in anything but small quantities, but it also means that loud firecrackers can be made with thin paper casings which are inexpensive and produce minimal debris. One of the earliest flash powder exploding devices to be granted a patent, Thomas Hitt's "Flashcracka" of 1918 (U.S. Patent No. 1,253,596), had no end plugs at all. It consisted of a thin paper bag of flash powder, tied to the fuse and placed in the center of a long tube. With only the air column at each end for confinement, this design was quite successful and was widely imitated by other manufacturers. Most flash crackers do have end plugs, but with good quality powder only thin paper ones are required. The Chinese quickly adapted their ancient firecracker technique to making small flash crackers, and billions of them have been produced. The only other difference from the old black powder version is that the ends do not need to be clayed or tied; with flash powder simply folding the paper in upon itself is enough. The colored outer paper, the tissue paper fuses and the method of braiding into flat packs are the same. Formerly, many different sizes were available, but increasing restrictions have limited them to 1½ inches in length in the United States, and even this size is not as heavily charged as it used to be. The smallest, called lady crackers or ladyfingers, are only ⅛" o.d. and less than an inch long.

At one time or another, flash crackers have been manufactured in most countries, with slightly different designs; for example those made in England were called "thunderflashes." Several styles are popular in Germany, under the general term "knallkörper." Instead of using a typical fuse, the most distinctive of these crackers have a rammed or pressed delay column which is topped off with a match head composition, in the manner used on some flares or torches. Unlike other firecrackers which are ignited from a flame or a smoldering "punk stick," these knallkörper are meant to be scratched on a match box and quickly thrown away.

One of the most famous American flash crackers was made with inner and outer paper cup sets to form an almost spherical casing. The assembled cups were made rounder by rolling them in a type of cement, usually a mixture of sodium silicate (waterglass) with chalk and zinc oxide, which produces a hard shell. Originally sold under the prosaic name "globe flash salutes," they became much better known as "cherry bombs." Since the casings were often colored red and the "stems" of visco fuse were usually green, the name is a particularly fitting one and remains a part of firework folklore to this day.

Probably the most notorious of all firecrackers is the "M-80," developed as an Army simulator for use in training exercises. There is amusing irony in the fact that a device so closely associated with delinquency and mayhem was originated by the federal government. Indeed, after World War II, military surplus M-80s were actually sold to the public by mail order. They were so well received that a civilian version was soon being manufactured, using the same famous name. The M-80 casing is a thin spiral-wound tube, 9⁄16" i.d. and 1½" long, usually red in color. The visco safety fuse enters through the side of the casing, and both ends have cup-shaped paper plugs glued in place. M-80s were well filled with high-grade powder and were very powerful for their size, but there is nothing unique about the basic design. Many similar crackers, both larger and smaller, also found a ready market. Silver salutes, for example, were slightly smaller than M-80s and were simply named for the color of the tubes. In addition to manufacturers' names, there are a great many slang terms for crackers of this type, such as "ash can." It is perhaps a comment on the changes in society that these devices became closely associated with juvenile delinquency. The massive cannon crackers of 1910 could destroy hands and arms, or even kill people outright, but most reformers at that time focused on accident prevention. Fifty years later, injuries were still an issue, but the emphasis was on deliberate vandalism, and all too often big firecrackers were deemed guilty by association. Mailboxes and trash cans were popular targets, and water-resistant visco fuses added further possibilities. One particularly dramatic stunt, perhaps more often the subject of "urban folklore" than actually perpetrated, was to flush an M-80 or cherry bomb down a toilet, where the explosion would burst pipes with spectacular results. In the United States, all the large flash salutes were banned from open sale by 1966. They are still available under permit for special purposes, such as frightening birds away from crops.

As with alcoholic beverages during the Prohibition era, and many other illegal drugs today, wherever a strong demand exists, there are usually people who will provide a supply. Flash crackers are among the easiest of all fireworks to make, and unless large quantities of powder are accumulated, they are quite safe for those who make them. Despite stiff, indeed ludicrous, penalties for selling them, black market or "bootleg" salutes are readily available in many parts of the United States. Some of them remain faithful to the old standards, while others have low-quality fuses, hard plugs, or powder leaks, and are more dangerous than the originals. Besides the universal M-80s, one hears of "bulldogs" (short and fat?), "blockbusters" (presumably big), and various arbitrary sizes such as the "M-100" and "M-200." Some come with names or sales pitches revealing how many it takes to equal the proverbial stick of dynamite. This is quite an achievement considering that true dynamite – as opposed to other blasting agents – has not been manufactured in the United States since the early 1970s, and even when it was made it came in many different strengths. Obviously there are no real standards for a product which is completely off the record, so the best advice for anyone who encounters bootleg salutes is to assume all of them to be dangerous.

The irrepressible appeal of large forbidden firecrackers has inspired some American companies to sell legal imitations. These pitiful frauds are usually made with red spiral-wound tubes and have various suggestive names such as "M-50," "M-70," and "M-88" or even "Baby Dynamite." Stillborn dynamite would be a better description, since all these items are subject to the same 50mg limit as the smallest Chinese crackers. Indeed, with the tiny powder charge scattered in an oversized casing, many of the pretenders are neither as loud nor as good as the ordinary one-inch firecracker. They are analogous to the "near beer" of the 1920s or the barely legal stimulant capsules sold in truck stops today, except that the underpowered booze and drugs probably don't really fool anybody. Due to government paternalism, there is a whole generation of Americans with very little idea how powerful a small firecracker can be. Grave warnings such as DO NOT HOLD IN HAND are mostly for show on the look-alikes, which are not even potent enough to break the skin. If people accustomed to these items encounter bootleg M-80s, or if the real thing should be legalized again, the false sense of security could prove disastrous. Furthermore, the look-alike salutes are very expensive compared with other 50-milligram firecrackers.

Torpedoes, in firework parlance, are not devices fired in the water. The name has been applied to many different items which explode from impact instead of requiring a spark or flame. Like other explosive fireworks, torpedoes were formerly manufactured in much greater variety and in larger sizes. For more detailed information, the reader should consult older works on pyrotechny by Weingart[249] and others, or the recent *Impact Firecrackers*[223] by A. J. Smith. Since many people do remember torpedoes, and they are still found in other countries, a brief description follows.

Toy paper caps are made with potassium chlorate and red phosphorus, which is the most unstable and sensitive mixture found in commercial fireworks. Specialized machinery for their manufacture is shown in Photo 15-13. One type of torpedo can be made with caps of this kind, larger than those sold for cap pistols, and surrounded by fine gravel. Similar compositions were sometimes used in torpedoes made of compressed clay or other substances.

Globe torpedoes were the most famous and powerful of the traditional kinds. They were made with the same type of paper cup sets used for cherry bombs and were coated in a similar manner, being tumbled in barrels while wet until they were almost perfect spheres. Compositions were usually based on potassium chlorate and antimony sulfide; this is much less sensitive than the chlorate/red phosphorus mixture. The greater weight of globe torpedoes, and the friction produced by the gravel filling, were enough to make them explode when thrown against a hard surface. Unfortunately, the gravel contributes to the hazards, and these potent torpedoes were restricted in many states even before federal law did away with all firecrackers of comparable size.

Cracker balls were small Japanese torpedoes of the globe style, containing a somewhat more sensitive mixture of potassium chlorate and arsenic disulfide (realgar) together with gravel.

Paper or silver torpedoes are made with silver fulminate, a primary explosive even more sensitive than the mercury fulminate once used in blasting caps and primers. The compound must be made in small quantities by firework makers as it cannot be shipped or stored in bulk. These torpedoes are mostly fine gravel; the only casing is a single layer of tissue paper, twisted shut to form a tail. In the United States they are the only survivors of the formerly large family of torpedoes. As might be expected, only the smallest are still permitted: the various brands of "poppers" or "snappers" contain only a quarter grain of fulminate, or about 15mg. They make a very sharp crack which displays the power and brisance of silver fulminate, but are mild enough that they can be crushed between the fingers without discomfort. Torpedoes are traditionally packed in sawdust to help prevent accidental explosion during shipping.

When more powerful torpedoes were marketed, they were understandably popular among children, and pranksters of all ages. However, torpedoes are rarely found on the underground market, probably because they require much more skill to make than flash crackers, and expose the people producing them to more danger.

Table 15-8. White Stars.

	1	2	3	4	5	6
Potassium nitrate	64	48	57	12	15	8
Barium nitrate	-	-	-	-	13	64
Potassium perchlorate	-	-	-	58	55	-
Sulfur	16	10	14	-	-	5
Antimony sulfide	11	-	21	9	-	-
Red gum	-	-	-	9	11	-
Aluminum, dark (U.S. Aluminum #809)	-	-	1.5	-	-	19
Meal powder	5	-	-	-	-	-
Calcium silicide	-	38	-	-	-	-
Charcoal	-	-	1.5	7	2	-
Dextrin	4	-	5	5	4	4
Gum arabic	-	4	-	-	-	-

NOTES: Formula 1 represents the oldest type of white star composition, such mixtures having been in use for centuries. Formerly arsenic sulfides (realgar, As_2S_2, and orpiment, As_2S_3) were used in lieu of antimony sulfide, and such stars were somewhat more readily ignited. Formula 2, with calcium silicide, represents an approach that had a vogue amongst the Italians some years ago, while Formula 3 is an attempt to brighten the traditional saltpeter and antimony white star by adding a small amount of aluminum. Formulæ 4 and 5 show the difficulty of achieving a white star with potassium perchlorate as an oxidizer. Because of the presence of chlorine in the flames as well as the flame temperature, such compositions have a tendency to show a violet or green tint, and must be carefully balanced, often depending upon the quality of available ingredients. Formula 6 is the traditional 'luce forte' with barium nitrate and aluminum (often mistaken for a magnesium star by the uninitiated). It ignites with difficulty and therefore requires heavy priming.

Pull crackers or "booby traps" have no fuses, and are distinguished by the long string which comes out both ends of the tube. In fact, a single piece of twine is doubled back on itself within the casing. These crackers depend on a highly sensitive mixture containing, among other things, red phosphorus. The composition is applied as a wet slurry to the loop of twine before it is rolled up tightly in the paper. When it is dry, the friction of straightening the twine is enough to make it explode. Pull crackers are used for practical jokes by tying the strings to a door, toilet seat, or other object which the intended "victim" is expected to move. A similar device is contained in party favors which scatter confetti when the exposed string is pulled.

Snakes

Pyrotechnic *snakes* are a familiar toy firework type depending upon the ability of a composition to burn producing a snake-like ash. Two unrelated chemistries have been employed to this end. The property of the thiocyanates of mercury to burn yielding a snake was first discovered by F. Wöhler in 1821.[44] Mercuric thiocyanate gives a better snake than does the mercurous salt. Such snakes have long been obsolete, banned because of concern over toxicity; current exaggerated fears have evidently banished the effect even from the chemistry classroom.

The version in common use today dates from an observation made in 1867 by G. Vorbringer about the burning properties of nitrated pitch. Published accounts suggest that the best product for the purpose is "naphthol pitch," a by-product of the manufacture of β-napthol, but ordinary coal tar pitch can be used. The nitration is done with fuming nitric acid to which a small quantity of water is added just prior to beginning the nitration.[139] The pitch is first pulverized, then mixed with linseed oil in a ratio of approximately 5 pitch to 1 linseed oil, and the combined materials are nitrated with anywhere from 60 to 120% of their weight of acid. Existing literature suggests that a process of "nitration by kneading" is used, but in current practice the nitration is carried out remotely. Some makers wash the nitrated pitch after this process while others do not.

The nitrated pitch will not burn on its own and requires an additive to sustain combustion. Depending upon the choice of additives, an afterglow reaction may be made to occur in the ash, resulting in a variant of the product sold under the name "glow worm." Shimizu[216] reports the first composition; the second was in use in the United States prior to the cessation of domestic manufacture of this article approximately 30 years ago.

Snakes

Nitrated pitch	75	49.5
Ammonium perchlorate	25	-
Tetryl (2, 4, 6-trinitrophenylmethylnitramine)	-	49.5
Graphite	-	1

Table 15-9. Red Stars.

	1	2	3	4	5	6
Ammonium perchlorate	-	-	-	-	-	28
Potassium chlorate	63	63	-	-	-	-
Potassium perchlorate	-	-	63	65	25	32.7
Strontium nitrate	-	-	-	-	20	-
Strontium sulfate	-	-	-	-	15	-
Strontium carbonate	21	18	16	15	-	16.8
Red gum	8	14	11	13	5	14
Shellac	3	-	-	-	-	-
Charcoal, air float	-	-	5	-	-	1.9
Lampblack	-	-	-	3	-	-
Chlorinated rubber	-	-	-	-	15	-
Magnalium, 50:50, 200-mesh	-	-	-	-	20	-
Hexamine	-	-	-	-	-	2.8
Dextrin	5	5	5	4	-	3.8

NOTES: Formulæ 1 and 2 represent conventional chlorate/resin stars, and Formulæ 3 and 4 are their perchlorate counterparts; all are dampened with water. Formula 5 is a brilliant metal-fueled type and is dampened with acetone; the chlorinated rubber serves both as chlorine donor and binder. Formula 6[16], with ammonium perchlorate, is dampened with water and requires a special, non-nitrate prime (see Formula 6, Table 15-16).

Aerial Fireworks

Stars and Garnitures

The familiar, colorful bursts of ærial fireworks depend on small pellets of consolidated composition called *stars*. Nearly all stars require an adhesive binder, which must be readily combustible without having a significant effect on the quality of the flame. The best binder depends on several factors, but the content usually does not exceed 5%. Exceptions occur when it is necessary to bind high percentages of bulky materials like lampblack or flake aluminum, or when a resinous fuel does double duty as a binder. At one time it was popular to add an adhesive solution, such as gum dissolved in water or shellac in alcohol, to the color composition. Today, the usual practice is to incorporate the proper amount of binder, in dry powder form, as part of each individual star composition, and to add only the solvent when the stars are to be made. Dextrin, a partially hydrolyzed starch, is easily the most popular of these binders in the United States. Other water-soluble binders include gum arabic and related plant gums, as well as glutinous rice starch which is the standard in Japan. Alcohol-soluble binders include shellac and red gum, already present as fuels in many color mixtures. Alcohol is normally avoided in modern commercial operations because of expense, regulatory complications, more difficult cleanup, and the danger of having work areas filled with potentially explosive fumes. However, it can be valuable with mixtures that might undergo undesirable reactions if dampened with water, or in situations where water would take an excessive length of time to dry. Solutions of nitrocellulose (in acetone, amyl acetate, or other organic solvents) have also come into use for compositions which react with water, especially those containing magnesium powder. Again, the expense and fire hazard limit commercial applications, but this technique is currently in common use for strobe or twinkling stars.

Star compositions may be broadly divided into color types and streamer or tailing types. The basic principles of color production do not differ from those seen in lances or flares, but as a rule, stars have faster burning rates. Because of this requirement, they often contain different fuels, more finely pulverized ingredients, or higher percentages of the more reactive oxidizers. Most colored stars are based on a chlorate or perchlorate with an organic fuel such as shellac, red gum, lactose, or rosin; in fact, when the term "color" is used in pyrotechny without any elaboration, it implies a mixture of this class. Despite the reactive nature of chlorates, colored stars do not ignite well from the brief flash of a lifting or bursting charge, and many of them can be blown out by wind until the flame is well established. Thus they need to be primed, typically with meal powder containing a small percentage of dextrin.

There are so many compositions for colors (Tables 15-8 through 15-14) that it is possible to mention only a few general guidelines here. Since the early nineteenth century when chlorates came into widespread use, a disproportionate number of firework factory accidents have been linked to them, especially when the mixtures also contained sulfur or sulfides. To some degree, the problem may

Table 15-10. Blue Stars.

	1	2	3	4	5	6	7	8
Potassium chlorate	62	65	64	62	-	-	-	-
Potassium perchlorate	-	-	-	-	61	62	39	46
Ammonium perchlorate	-	-	-	-	-	-	29	-
Copper acetoarsenite	21	-	-	-	-	-	-	-
Copper oxychloride	-	16	19	-	-	12	-	-
Black copper oxide	-	-	-	13	-	-	-	20
Basic copper carbonate	-	-	-	-	12	-	14	-
Sulfur	-	-	-	-	-	18	-	-
Red gum	-	-	-	9	9	-	14	5
Vinsol resin	-	-	5	-	-	-	-	-
Lactose	-	10	-	-	-	-	-	-
Stearin (stearic acid)	8	-	2	-	-	-	-	-
Hexachlorobenzene	4	-	-	-	-	-	-	-
Polyvinyl chloride	-	5	-	-	-	-	-	-
Chlorinated rubber	-	-	-	11	13	-	-	18
Dechlorane	-	-	-	-	-	4	-	-
Chlorinated paraffin	-	-	5	-	-	-	-	-
Magnalium 65:35, 100-mesh	-	-	-	-	-	-	-	6
Dextrin	5	4	5	5	5	4	4	5

NOTES: Formula 1, with Paris green, is typical of the compositions widely used in the mid-twentieth century. Paris green will give a useful blue color even without a chlorine donor, and with one, an excellent color, as well as a large flame and easy ignition. Formulæ 2, 3, and 4, with potassium chlorate as oxidizer, and Formulæ 5[217] and 6, with potassium perchlorate, show various approaches to the replacement of toxic Paris green. Formula 7[139] is an example of the use of ammonium perchlorate, which results in a fine color, but requires a special prime (*e.g.*, Formula 5, Table 15-16). Formula 8 is a bright blue with a small amount of metal fuel.

be described as a "learning curve," since almost any color mixture is more dangerous to handle than black powder, and some of the early accidents occurred because of the use of open flames for heating or illumination, which is obviously foolhardy in the presence of any kind of firework composition. Unfortunately, some chlorate/sulfur stars did ignite spontaneously during drying, or from relatively mild friction. This was often traced to improperly washed sulfur which contained acid, or to soured gum solutions (also acidic); in a few cases the culprit was hard water, which led to the formation of unstable calcium chlorate. With proper knowledge, it is not too difficult to prevent these problems, but they were prevalent enough to cause a strong reaction against chlorate/sulfur mixtures. Indeed, they were banned in Britain so long ago as 1894. Exaggerated warnings about these old compositions are sometimes disseminated by persons who appear to have no practical experience with them. For example, one often reads that chlorate/sulfur stars cannot be used in ærial bombshells because they are too sensitive to withstand the shock of the lifting charges. This would have been news to the Victorians, as it would be to the modern-day Japanese, who occasionally use such mixtures in some of their best chrysanthemum shells, which they reserve for their own exhibitions. Another warning that is often repeated, but seldom explained, is the notion that it is unacceptable to mix chlorates with sulfates, for no apparent reason other than the fact that sulfates contain sulfur. Problems have occurred with copper sulfate, as mentioned before, because this salt is strongly acidic in the presence of moisture. However, the sulfur in sulfates is already completely oxidized, and cannot behave as a fuel, and there is no logical reason to expect unwanted reactions with sulfates which are insoluble or which have a pH near neutral. Chlorate color mixtures containing free sulfur are a different story; most professional pyrotechnists consider them obsolete and avoid using them. At best, they are about twice as sensitive to shock as chlorate stars which lack sulfur.* In nearly all cases it is possible to make excellent colors without them.

Aside from questions of stability and price, some fuel combinations simply work better than others. Shellac has long been viewed as one of the best fuels in chlorate stars, but its high cost has limited its use, and shellac does not burn well with potassium perchlorate despite the latter's high oxygen content. On the other hand, a mixture of potassium chlorate, red gum, strontium carbonate and dextrin can be converted to use potassium perchlorate without much change in performance. Copper compounds tend to have a catalytic effect which increases burning rates; this is especially important in perchlorate mixtures and perchlorate blues have become common. Charcoal dust is often added in small percentages to both chlorate and perchlorate stars to improve ignitability and increase burning speed, but too much charcoal impairs the colors. Stearic acid may be used in small percentages to increase flame size, but it usually does not perform well as the main fuel – except in traditional chlorate blues containing Paris green (itself a fuel to some extent), where the stearin burns rapidly and smoothly. Rosin is

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* drop hammer test results, per Shimizu[215]: $KClO_3$ 70%/Lactose 30%: 43 cm drop
$KClO_3$ 70%/Sulfur 30%: 23 cm drop

Table 15-11. Green Stars.

	1	2	3	4	5	6	7	8
Barium nitrate	39	-	34	30	56	45	-	-
Barium chlorate	27	50	-	-	-	-	32	36
Potassium chlorate	16	28	-	-	-	-	32	-
Potassium perchlorate	-	-	38	44	-	18	-	30
Paris green	-	-	-	-	-	-	20	-
Basic copper carbonate	-	-	-	-	-	-	-	11
Red gum	13	6	11.5	13	7	6	-	13
Shellac	-	6	-	-	-	-	8	-
Charcoal, air float	-	4	11.5	4	-	3	-	-
Magnalium 75:25, 200-mesh	-	-	-	-	17	-	-	-
Magnalium 50:50, 200-mesh	-	-	-	-	-	11	-	-
Polyvinyl chloride	-	-	-	5	15	-	-	-
Chlorinated rubber	-	-	-	-	-	12	-	6
Stearin	-	2	-	-	-	-	4	-
Dextrin	5	4	5	4	5	5	4	4

NOTES: Formulæ 1 and 2 make use of barium chlorate with its ability to produce excellent green color, while addressing problems of expense, slow burning rate, and sensitivity to shock and friction by blending it with other oxidizers. Formula 2 is especially adapted for pumped stars, but may be used for all types. Formula 3 is an inexpensive and relatively safe mixture but the color is poor. Formula 4, utilizing a chlorine donor, represents a slight improvement; Formulæ 5 and 6 show how chlorine donors combined with metal fuels can be used to create good green color without barium chlorate. Formulæ 7 and 8 are turquoise or aquamarine effects.

another fuel which has a very high oxygen demand and is normally used only in small percentages. A partially oxidized rosin called "Vinsol™*" is commonly available, and for most purposes, the two materials may be considered interchangeable. Synthetic resins find much less use in fireworks than in military devices. One exception is the phenolic type, which has good burning characteristics in perchlorate mixtures. Resorcinol-formaldehyde resins have been used to a limited extent, but phenol-formaldehyde resins are less expensive and are available in greater variety, including powder form. The archetype of this group is Bakelite, used since 1907 for such items as electrical switches and screw-on bottle caps. If the medium is alkaline and the ratio of phenol to formaldehyde is less than 1:1, the result is a "resole" resin, such as Bakelite. Reaction of phenol with formaldehyde in a ratio greater than 1:1 under acid conditions produces thermoplastic resins called "novolacs," the type normally used in pyrotechnics. Some of these materials are photoreactive and also tend to reagglomerate if stored for long periods; consequently they are often kept in large pieces and ground as needed for use. The pyrotechnic properties of these resins are discussed by Shidlovskii[214] under the name "Iditol." In recent years they have been extensively used by the Chinese and have also been adopted in some other firework producing countries, notably Brazil.

Blue stars have a reputation for being difficult to make, and this has probably been over-emphasized. It is true that a good deep blue requires more attention to the quality and proportions of the ingredients than most other colors, but there are many published recipes which work well. Purple is the only common star color which is mixed like an artist's paints; that is, purples depend on a delicate balance between the red light of strontium and the blue of copper. In some cases, a change of less than one percent in the ratios can have a significant impact on the color. Many shades of purple and violet were used in the nineteenth century; the color languished for a time but has made something of a comeback. Some types of color compositions give excellent results over a broad range of mixture ratios. A good example is provided by these deep red effects recommended by Weingart[249]:

	Parade Torches	**Box Stars**	**Cut, Pumped or Candle Stars**
Strontium nitrate	16 (59.3%)	3 (41.4%)	6 (38.7%)
Potassium chlorate	8 (29.6%)	3 (41.4%)	6 (38.7%)
Shellac	3 (11.1%)	1 (13.8%)	1 (6.5%)
Fine charcoal	-	-	2 (12.9%)
Dextrin	-	¼ (3.4%)	½ (3.2%)

Colored stars which contain fine aluminum or magnesium powders, or an alloy of the two, burn more brightly and may be called "electric" or simply "brilliant" stars. Electric stars are sometimes made with nitrate oxidizers only, and chlorine donors as necessary. Such compositions are essentially the same as those used in military signals. Storage concerns and difficult ignition limit their use in

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* Trademark of the former Hercules Powder Co.

Table 15-12. Yellow Stars.

	1	2	3	4	5
Potassium chlorate	76	-	-	-	-
Barium nitrate	-	-	64	62	29
Potassium perchlorate	-	68	-	-	29
Sodium oxalate	10	9	-	-	-
Cryolite	-	-	8	8	9.5
Magnalium, 50:50, 200-mesh	-	-	-	-	9.5
Aluminum, dark (U.S. Aluminum #809)	-	-	19	18	-
Sulfur	-	-	5	4	-
Shellac	-	8.5	-	-	-
Vinsol resin	4.5	8.5	-	-	-
Red gum	4.5	-	-	-	7
Lampblack	-	2	-	-	-
Polyvinyl chloride	-	-	-	2.5	-
Chlorinated rubber	-	-	-	-	12
Dextrin	5	4	4	5.5	4

NOTES: Formulæ 1 and 2 are simple chlorate and perchlorate stars respectively, showing adjustments in the resin fuels to 'tune' the color to taste. Formula 3 is a variant on its white counterpart (Formula 6, Table 15-8), equally brilliant and difficult to ignite, requiring a hot prime. Formulæ 4 and 5 illustrate the use of a chlorine donor to encourage formation of barium monochloride in the flame, balancing the amber of the sodium and tilting the color towards a desired 'lemon yellow.'

commercial fireworks. Plain white stars, without metal fuels, are traditionally made with saltpeter, sulfur, and antimony sulfide or realgar, often with small percentages of meal powder and other ingredients. Pure white stars, even without arsenic, are uncommon today and good ones are more likely to catch the eye of a pyrotechnist than the highly publicized blue. Traditionalists do not consider these color stars, but in most cases they are not tailed stars either.

Perchlorate stars have become increasingly common in some places, and there are those who actively discourage the use of chlorates even with resin fuels. Chlorate stars are barred from consumer fireworks in the United States, but are still common in display fireworks. Perchlorate stars are more difficult to ignite and usually burn more slowly; they produce a smaller flame from a given size star, and in some cases, the color is simply not as good. Stars containing potassium perchlorate and sulfur have occasionally been used but never became very popular. Current enthusiasts of perchlorate stars often bolster their performance with catalysts, metal powders, or reactive organic fuels such as benzoates, but these materials increase sensitivity as well. Pyrotechny in general, and making colors in particular, are good illustrations of the cliché, "there's no such thing as a free lunch." This is even more true of the ammonium perchlorate stars which are popular among firework hobbyists. Unlike the potassium salt, ammonium perchlorate readily produces deep colors with good flame size. But in addition to the other disadvantages of perchlorates, the ammonium salt causes problems with the most common material in fireworks, black powder. Ammonium perchlorate reacts with saltpeter to produce ammonium nitrate, which attracts water and renders the material unignitable. Stars made with this oxidizer often require at least two different kinds of priming (Table 15-16). Typically, a mixture of potassium perchlorate and resin fuel, perhaps with a small percentage of silicon or aluminum powder, is coated on the ammonium perchlorate stars. After this is dry, a black powder prime is added to ignite the potassium perchlorate prime. At least one of these priming layers should be bound with a non-aqueous system, such as nitrocellulose lacquer, or the ammonium nitrate problem is likely to occur in spite of the intermediary layers[220]. Ammonium perchlorate mixtures are not immune from spontaneous combustion. Unwanted reactions are particularly common in mixtures which contain magnesium, and the best way to prevent them is to bind the whole star with nitrocellulose. In addition, the magnesium or magnalium must be given a surface treatment to protect it against corrosion. The most common method employs potassium dichromate. For every 1000g of metal, 50g of potassium dichromate is dissolved in 300 ml of hot water. This solution is intimately mixed with the metal, and the latter then dried by heat, with frequent stirring to prevent formation of lumps[220]. Additional dichromate is added to the composition to buffer it against reaction. Since potassium dichromate is an irritant poison, an alternative coating method using ammonium metamolybdate $[(NH_4)_6Mo_7O_{24}]$ and ammonium dihydrogen phosphate $[(NH_4)H_2PO_4]$ has been recommended[2]. This is reported to give corrosion protection superior to that afforded by dichromate treatment. As might be expected, manufacturers are unwilling to perform these additional and bothersome steps except where there is

Table 15-13. Purple and Violet Stars.

	1	2	3	4	5	6
Potassium chlorate	63	60	-	28	23	-
Potassium perchlorate	-	-	64	36	30	46
Strontium nitrate	-	-	-	-	10	-
Strontium carbonate	10	14	8	8	-	13
Copper oxychloride	7	-	-	4	19	-
Basic copper carbonate	-	8	-	-	-	-
Black copper oxide	-	-	5	-	-	8
Lactose	-	7	-	-	-	-
Red gum	-	2	9.5	10	5	5
Shellac	11	-	-	-	-	-
Polyvinyl chloride	-	5	-	-	-	-
Hexachlorobenzene or Saran	5	-	-	-	-	-
Chlorinated rubber	-	-	9	10	10	17
Magnesium, 200-mesh	-	-	-	-	3	-
Magnalium, 65:35, 100-mesh	-	-	-	-	-	6
Dextrin	4	4	4.5	4	-	5

NOTES: Formula 1 is an excellent color, slower-burning and more difficult to ignite than its use of potassium chlorate might suggest. Formula 2 is easier to ignite but its color is not so deep. Formula 3[217] with potassium perchlorate is due to Shimizu. Formula 4, of similar type, replaces some of the perchlorate with chlorate in an attempt to improve ignition and enlarge the flame. Formula 5 (dampened with acetone) is a metal-fueled composition in which the chlorinated rubber serves as binder and protects the strontium nitrate against moisture as well as acting as a chlorine donor. Formula 6, with magnalium replacing magnesium, is a bright purple that may be dampened with water.

a compelling reason to do so. Ammonium perchlorate is employed mainly in metal-fueled compositions, and most of what is used by firework manufacturers goes into strobe or twinkling stars (Table 15-17). The compositions, which contain magnesium or a magnesium/aluminum alloy (magnalium), burn in an oscillatory two-stage reaction: a "dark" phase which is barely visible, punctuated by a brilliant "flash" phase – resembling a strobe light. Other oxidizers can be used in strobes, but ammonium perchlorate produces an especially wide range of good colors. Normally, the mixture also contains a sulfate of the appropriate metal, such as sodium for yellow flashes or strontium for red. The ammonium perchlorate sustains combustion during the cooler "dark" phases, while in high-temperature reactions with magnesium, sulfates also function as oxidizers. Strobe stars are usually small and are not used in great quantities compared to other shell components. Thus the difficulties of working with ammonium perchlorate and organic solvents are not as bothersome as they would be with ordinary colored stars.

Tailed stars contain an excess of fuel in the form of charcoal, lampblack, or such metals as aluminum, titanium, ferro-titanium, steel filings, and zinc dust. Most stars in this group use saltpeter as an oxidizer – in fact, some of them contain commercial meal powder – and these require little or no priming. In general, the mixtures resemble those used in fountains, except that stars contain a binder. As with colors, there are often "families" of streamer compositions, where the greatest difference between two effects is the burning rate. For example, a star containing 35% saltpeter and 50% charcoal dust (with sulfur and a binder) burns quite slowly with a long, subtle tail, and is typical of "weeping willow" effects. With 48% saltpeter and 40% charcoal, combustion becomes much livelier and the mixture is suitable for chrysanthemum shells, or for all-purpose gold stars to be mixed with color effects. With 70% Meal D, 25% charcoal and 5% dextrin, even a large one-inch square star burns in less than two seconds. When properly made, such stars leave thick, bushy tails and can be used with extra-powerful bursting charges to produce a "spider" effect. Even seemingly simple stars like the charcoal types (Table 15-18) are subject to great variation in quality, depending on the mixing technique, final moisture content and other factors. Charcoal itself is a major variable; many different types are used by firework makers and those which give the greatest propulsive force in gunpowder or rocket mixtures are not necessarily those which are best for producing sparks. Pine charcoal is highly regarded for streamer mixtures in Japan, but in the United States most manufacturers depend on a commercially available charcoal made from a variety of hardwoods, including maple and hickory. It is a general-purpose product which does not give top performance in most firework applications, but is reasonably consistent in quality. Metal powders are chemically simple but are subject to wide variation in particle size and shape; this is especially important with aluminum. Iron and steel filings are more seldom used in commercial fireworks than the older literature might lead one to believe, mostly because they have to be specially treated to prevent corrosion. Today when it is desirable to have gold sparks brighter than those of charcoal, a common practice is to use aluminum, or an alloy of iron with

Table 15-14. Orange Stars.

	1	2	3
Potassium chlorate	76	-	-
Potassium perchlorate	-	58.5	47
Sodium oxalate	4	12.5	-
Cryolite	-	-	4.5
Calcium carbonate	-	-	11
Strontium carbonate	4	-	-
Strontium oxalate	-	4	-
Rosin	4	17	-
Red gum	8	-	6.5
Magnalium, 50:50, 200 mesh	-	-	11
Chlorinated rubber	-	4	15.5
Dextrin	4	4	4.5

NOTES: Formulæ 1 and 2 achieve an orange color by combining the red of strontium with the yellow of sodium, while Formula 3 makes use of the pinkish-orange of calcium together with sodium yellow. Such composite colors require careful balancing, often to suit particular lots of ingredients, in order not to appear simply to be bad reds or yellows.

Table 15-15. Zinc Stars.

	1	2	3
Zinc dust	62	45	71
Potassium nitrate	21.5	30	-
Potassium chlorate	-	-	9
Potassium perchlorate	-	-	18
Meal D	-	15	-
Charcoal, air float	11	5	-
Sulfur	4	-	-
Dextrin	1.5	5	2

NOTES: The blue-green flame color produced by compositions containing elemental zinc has been known to pyrotechnists since the eighteenth century; it was mentioned by Lavoisier[142]. Formula 1 is Weingart's[249] 'granite star.' Formula 2 is a comparable nitrate-based mixture, while Formula 3 represents the 'electric' type with chlorate and perchlorate.

titanium, which does not rust, in combination with black powder or its ingredients (Table 15-19). Some tailed stars are based on chlorates, perchlorates or barium nitrate, and must be primed like colored stars; those containing high percentages of flake aluminum can be particularly difficult to ignite. These tend to burn more brightly because of the higher flame temperature (Table 15-20). Some stars have a double effect, combining a distinctly colored head with a trail of sparks. Most of these contain chlorate or perchlorate, but one very old type is made with zinc dust and black powder ingredients. Good zinc stars (Table 15-15) are blue-green with tails of delicate charcoal gold, and seem rather exotic today. Turquoise or aquamarine colors, with or without tails, are hardly ever seen in the more modern types of compositions; examples may be seen in Formulæ 7 and 8, Table 15-11.

One specific type of tailed star which deserves further discussion is the tremalon or "glitter" effect (Table 15-21). These compositions burn with a dull yellowish flame, scattering molten droplets of dross. The droplets or "spritzels" then react with bright flashes, at a distance from the star itself. A star moving through the air leaves a sparkling, flickering tail different from those produced by other types of streamers. In general, the flashes may be classified as white or gold, although off-white and pink are occasionally seen. The delay time between the main flame and the secondary reaction can vary over a wide range, and there may be a great many small flashes or only a smattering of large ones. Although this phenomenon is subject to dozens, if not hundreds, of variations, the successful compositions fit rather narrow parameters. All of these mixtures are based on black powder ingredients, with the addition of aluminum. The metal may be in flake or atomized form, and is usually between 100 and 325 mesh, somewhat coarser than that used in flash powders or illuminating stars. Magnalium alloys are sometimes used and can add a distinctive sizzling sound to the visual effects, but magnesium alone does not work. Aluminum content in tremalon mixtures is usually between 5% and 10%. In some cases, a small percentage of coarser flake aluminum is included; this does not enter into the spritzel reaction, but merely burns, as it would in any other tailed star. Good tremalon compositions usually contain antimony sulfide, although in a few of them, another sulfide or additional elemental sulfur is used. The exact mechanism of the reaction is a matter of debate, but it is probable that the formation of molten potassium sulfide plays an important rôle. Many additives, notably oxalates and carbonates, are used to increase delays or otherwise to enhance the performance. Sodium oxalate is one of the most popular ingredients, and usually lends a gold color to the flashes.

The effect under discussion was apparently discovered around the beginning of the twentieth century, when aluminum came into widespread use in pyrotechny. Italian (or Italo-American) workers named it *tremolante** for its trembling or quivering appearance, and this word was quickly anglicized to "tremolan" or

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* From the Italian *tremolare,* meaning, *inter alia,* to twinkle, as do the stars of the firmament:

"Anco in Ciel le stelle tremule..."

[Ansaldi, *San Giovanni Battista*]

Table 15-16. Star Primes.

	1	2	3	4	5	6	7
Potassium nitrate	75	66	64	35	-	-	38
Potassium perchlorate	-	-	-	35	74	37	-
Charcoal, air float	15	16	13	25	6	30	-
Lead tetroxide (red lead, Pb_3O_4)	-	-	-	-	-	22	-
Silicon	-	-	-	-	-	7	38
Sulfur	10	13	8.5	-	-	-	-
Rosin	-	-	-	-	12	-	-
Potassium dichromate	-	-	-	-	5	-	-
Aluminum, dark (U.S. Aluminum #809)	-	-	-	-	3	-	-
Ferro-titanium, 100-mesh	-	-	9.5	-	-	-	-
Meal D	-	-	-	-	-	-	19
Dextrin	-	5	5	5	-	4	5

Notes: Many stars, particularly those based on black powder (or its ingredients) or those using chlorates as oxidizers, require little or no priming to ignite; a dusting with a simple, hand-mixed composition of a black powder type, either without (Formula 1) or with dextrin (Formula 2) serves to prevent their sticking to each other while damp. Formula 3, containing ferro-titanium, is a 'hotter' prime for stars more difficult to ignite; Formula 4, without sulfur, may be used if it is desired to prevent chlorate/sulfur contact, and also as a suitable 'changing relay' in round stars. Formulæ 5[228] and 6[16], without potassium nitrate, are used for stars containing ammonium perchlorate, to prevent the formation of hygroscopic ammonium nitrate. Formula 7 is an adaptation of a military 'hot' prime containing silicon.

"tremalon." In plain English, "glitter" is an apt description and has become the most common term, except among some people in the industry. More recently there have been several essays written on this phenomenon, exploring both practical and theoretical aspects[256]. These writings have reinforced the use of the term "glitter," but unfortunately have expressed dogmatic and confusing ideas about the term "flitter." There are now many writers who use the word "flitter" to mean specifically an effect with a large excess of metal fuel, in coarse particles which simply burn in the air (*e.g.*, Formulæ 2 and 3, Table 15-20). Thus they argue that "flitter" is completely different from "glitter," with its molten droplets and delayed flashes. The trouble with this distinction is that the term "flitter" already had a long history of use by working pyrotechnists, and was often applied to compositions in the tremalon class. By any name, tremalon stars are beautiful and versatile. They are brighter than charcoal streamers without being so bright as to overpower good colored stars, and they harmonize well with most other ærial effects.

Another type of delayed spark is seen in "firefly" or "transformation" stars (Table 15-22). These are sometimes called charcoal/aluminum stars by experienced fireworks men on account of their principal ingredients. The aluminum content is quite low, around 5%, and in the form of coarse flakes. On the other hand, the charcoal content is very high, typically 40%, and at first, these stars appear to be simple charcoal streamers. The secondary effect resembles a tremalon with an extremely long delay, but there are significant differences between the two types of mixtures. "Firefly" compositions do not contain antimony sulfide or high percentages of sulfur, and do not produce large droplets of molten dross. When the aluminum flakes finally ignite, they do not react with brief flashes, but continue to glow and flicker for a considerable length of time. As in many pyrotechnic mixtures, the kind of charcoal is significant; in this case a high mineral content promotes the effect and it is possible to enhance it by adding a small amount of barium or strontium sulfate[218]. These stars are at their best in large shells and rockets, since the "fireflies" may persist for 30 seconds or more. They provide one of the longest duration effects which can be achieved in ærial fireworks without resorting to parachutes or balloons.

The *crackle* phenomenon, introduced by the Chinese, has been widely used and is discussed in two recent articles[121, 219]. It is based on the thermitic reaction of lead, copper, or bismuth oxides with magnesium/aluminum (magnalium) alloys, which bears some resemblance to the strobe effects discussed earlier; upon ignition a smoulder reaction begins in which the magnesium is consumed, followed by a flash reaction (the "crackle") involving the aluminum. Small micro-stars or granules of the thermitic compositions are mixed with a gunpowder-type composition to form stars (Table 15-23).

Cut stars (Photo 15-14) are roughly cubic in shape and are very common in the United States. Their sharp edges and corners make them easier to ignite, at least in theory, but their most important advantage is that they can be produced quickly with a minimum of equipment. To make stars of this type, the composition must be mixed with enough solvent to form a pliable mass resembling

Table 15-17. Strobe (oscillatory-burning) Stars.

	1	2	3	4	5	6	7	8
Barium nitrate	51	54	-	-	-	-	-	-
Ammonium perchlorate	-	-	57.1	57.1	48.1	45.2	47.5	47.6
Potassium nitrate	8	-	-	-	-	-	-	-
Barium sulfate	-	-	14.3	-	-	17.6	-	-
Barium carbonate	-	-	-	-	-	9.8	-	7.6
Strontium sulfate	-	-	-	11.4	15.4	-	-	-
Strontium carbonate	-	-	-	7.6	9.6	-	-	-
Calcium sulfate	-	-	-	-	-	-	12.4	-
Calcium carbonate	-	-	-	-	-	-	7.6	-
Sodium sulfate	-	-	-	-	-	-	-	12.4
Potassium dichromate	-	-	4.8	4.8	1.9	2	4.8	4.8
Magnalium, 50:50, 60-mesh	13	12	-	-	-	-	-	-
Magnalium, 50:50, 100-200 mesh granular	-	-	23.8	15.2	-	-	-	-
Magnesium, 100-200 mesh atomized	-	-	-	-	17.3	17.6	22.9	-
Magnesium, 100-mesh granular	-	-	-	-	-	-	-	23.8
Sulfur	23	20	-	-	-	-	-	-
Polyvinyl chloride	-	-	-	-	4.8	4.9	1	3.8
Hexachlorobenzene	-	9	-	-	-	-	-	-
Chlorinated rubber	-	-	-	3.9	2.9	2.9	3.8	-
Dextrin	5	5	-	-	-	-	-	-

NOTES: Formulæ 1 and 2 are dampened with water and cut small (under ¼") or rolled into small cores for round stars. The magnalium need not be treated. Formulæ 3 through 8 require the metal powders used to be treated with potassium dichromate. Formula 3, due to Shimizu[220], and formulæ 4-8, from Meinhart[164], are dampened with a 10% solution of nitrocellulose in acetone, then cut into 7/16" cubes. After drying, they are primed with Formula 5, Table 15-16, in a vehicle of nitrocellulose solution; after this has dried, finally primed with a thin black powder coat. Formula 3 may be given a faster frequency by replacing the barium sulfate with anhydrous magnesium sulfate. The resultant fast strobe is sometimes called a "shimmer" effect.

cookie dough or modeling clay. With dextrin-bound mixtures, this usually requires water in the amount of ten to fifteen percent of the weight of the dry composition, and occasionally even more. The proper amount for each kind of star can only be ascertained by experience. It is important to knead the mixture thoroughly, and it is usually a good idea to reserve some dry composition in case too much water is added. Once the proper consistency is achieved, the dough can be formed into slabs for cutting. In large quantities, it is normally first pressed or pounded into a wooden box to form a block or cake, from which slices of suitable thickness may be cut. Smaller quantities can be pressed into a star frame, which is only the height of one star and rests directly on the cutting surface. In some cases – especially with non-aqueous solvents that dry rapidly – the mixture may simply be spread on the cutting surface with a spatula or roller. After the slab of composition is in place, it is cut into cubes with a straight-edge knife. Ordinary color stars are often dusted with meal powder at this point; those requiring more elaborate priming are usually primed after they are dry. The freshly cut stars are transferred from the cutting surface into drying screens or trays lined with paper. Cut stars typically range from ¼" to ½" on a side, but they can be almost any size. Very large ones made of fast streamer compositions are used for spiderweb and palm tree shells. Cubes of ⅛" or less are sometimes made for use in fountains, or as cores for rolling round stars. In some of these applications consistent size is important, but ordinary shells work well with stars which are quite irregular in size.

Not all stars cut equally well, and there are some otherwise excellent compositions which are simply not suitable for this process. Most of the difficulties in making cut stars are related to the high water content required. Some stars, notably those containing strontium nitrate or sodium salts, take an excessive length of time to dry and may undergo undesirable reactions in the meantime. Compositions that contain high percentages of fine, dense powders are especially finicky about water content, and adding 14% instead of 12% may mean the difference between crumbly stars and a gooey mess which is all but impossible to cut. High percentages of bulky lampblack or flake aluminum can also be troublesome, either by being difficult to bind or by clinging to the knife and work surfaces. Often these problems can be solved by dampening with flour paste instead of water, or by using a non-aqueous binding system, but with some compositions, it is best to choose another form of star.

Pumped stars or cylindrical stars usually have a height about the same as their diameter, or a little greater. The star "pump" which gives them their name consists of a slotted tube and a close-fitting plunger (Photo 15-15). Small stars are adequately consolidated by simply pressing the pump assembly into dampened composition by hand. Larger ones require malleting or pressing like that used to load paper casings. As a rule, an excess of composition is pressed; the plunger can then be depressed until the pin stops on the edge of the sleeve. This determines the length of the star (some plungers have movable pins to allow different lengths to be made) and the excess can be cut off with a knife. With the star fully formed, the plunger is turned so that its pin engages the slot in the sleeve, and

Table 15-18. Charcoal Streamer Stars.

	1	2	3	4	5
Potassium nitrate	55	55	27	57	62
Charcoal, air float	30	27.5	16	16	11
Charcoal, 80-mesh	-	-	5.5	-	-
Charcoal, 36-mesh	-	-	-	12	-
Sulfur	8	10.5	9	10	16
Meal D	-	-	36	-	-
Lampblack	-	1	-	-	5.5
Dextrin	7	6	6.5	5	5.5

NOTES: Simple alteration of the proportions of ingredients, of the source or granulation of the charcoal, or of mixing techniques, leads to a wide variety of effects from compositions of this type, though they may appear quite similar on paper. Ball-milling or stamping the compositions was often practiced in the past, but the same results may be obtained by adding commercial meal powder, as in Formula 3.

the star can be pushed out and placed in a drying area. Obviously this method is far more time-consuming than making cut stars, so it is only used where there is some significant advantage in doing so. The most common reason for choosing a cylindrical star is when it is to be used as a single projectile in a tube. In the days when Roman candles had a much larger share of the consumer fireworks market, great quantities of small cylindrical stars were required. They were often made by packing dampened composition into "star plates" — metal or plastic plates drilled with dozens or hundreds of holes. The stars were ejected by means of other plates fitted with the corresponding number of pegs. Because these stars were already being turned out by the thousands, they were commonly used in rockets and mines, as well as candles. However, even the plate method is quite labor-intensive and requires more investment in tooling than most other star manufacturing techniques. It is almost a thing of the past, and today most American firework companies do not even make 1/4" or 3/8" pumped stars.

Large pumped stars are another matter; not only are they essential in exhibition-size Roman candles and other tube items, they are also very useful in shells. When making these stars, the composition does not need to be dampened as much as for cut stars – indeed it is counterproductive to do so. Some star compositions can be consolidated dry under high pressure, notably the military types discussed elsewhere in this book. Those used in display fireworks are typically mixed with 5% to 8% water, which is not enough to form a dough but leaves the mixture damp enough to stick together when squeezed by hand. The lower moisture content reduces the likelihood of chemical reactions, and decreases the drying time. These advantages become more and more significant as the star size increases. Many pumped stars are made of black powder mixtures which require no priming. Those which do need to be primed are usually placed in a bowl after drying, sprayed with water, and sprinkled with priming powder to coat them all over. Large pumped color stars are sometimes primed on the ends only, using a slurry technique.

Pumped stars made of tailed compositions are called *comets*; their applications range from small paper mortars which fire a single star to the largest ærial shells. Charcoal streamer mixtures are the mainstay, and the glitter or tremalon type is also very popular. Some comets are made of heterogeneous mixtures, such as magnalium crackling granules embedded in a matrix of charcoal composition. Less commonly, granulated black powder is included in a perchlorate/aluminum streamer to improve ignitability and give a better spread to the tail. For obvious reasons, such conglomerates are awkward for making cut or rolled stars, but a pump compresses them into dense, smooth pieces. Compositions containing iron, titanium, or their alloys are usually avoided in comets because they tend to scratch and "seize up" the pumps. Comets up to about 1½" diameter can be made well by hand ramming, but larger ones are sturdier and more consistent if made on an hydraulic press. Comets made to fit three-inch mortars are common, and in exceptional cases they can be as large as eight inches. In the larger sizes, pasted paper wrapping is often applied to comets to increase their strength, or to limit the burning surface for a longer duration.

Table 15-19. Bright Streamer (nitrate/metal) Stars.

	1	2	3	4	5
Potassium nitrate	59	-	11	54	-
Charcoal, air float	18.5	-	-	25	4
Sulfur	7.5	-	-	7	-
Aluminum, bright (U.S. Aluminum #808)	7.5	-	-	-	-
Aluminum, dark (U.S. Aluminum #809)	-	17	-	-	-
Aluminum, dark (German black)	-	-	17	-	-
Meal D	-	67	56	-	66
Barium nitrate	-	9	-	-	-
Titanium, 20-40 mesh	-	-	-	7	25
Wheat flour	-	-	11	-	-
Dextrin	7.5	7	5	7	5

NOTES: These compositions demonstrate the range of spark tails, from bright gold to off-white, that can be obtained by using powdered metals with nitrates as oxidizers. Formulæ 1 and 4, containing large quantities of charcoal and no commercial meal powder, give an effect resembling a brighter version of a charcoal star, whereas Formulæ 2, 3, and 5, in which the principal or total oxidizer content is found in the commercial meal, are both more brilliant and more fiercely burning.

There are many types of fancy comets designed to produce multiple effects; all of these require paste-wrapping and are quite time-consuming to make. One kind is the "married," "stacked," or color-tipped comet, in which an ordinary solid comet is attached to a chlorate or perchlorate colored star of the same diameter (Photo 15-16). Because of the difference in burning rates, the color segment is normally a "wafer" the height of which is less than its diameter. After being glued together, the married comet is wrapped in pasted paper (leaving both ends exposed) so that it will not come apart under the stress of a lifting or bursting charge. Finally, the color end must be primed.

If the plunger in a comet pump has a reduced diameter portion on the end, the stars made will have cavities which can accommodate secondary effects. The most popular of this class is the *crossette* or splitting comet. The hole in a crossette is relatively small in relation to the size of the comet; for example, a typical 1½" pump leaves a hole ½" diameter and ¾" deep (Photo 15-17, cross-section of crossette). After the explosive bursting charge is inserted, pastewrap is applied, leaving only the solid end and a small portion of the side exposed. Thus the solid portion (below the cavity) functions as a delay element as the comet streams through the air. The explosive component is subject to much variation from maker to maker. One very effective method uses a paper-cased "shot" which resembles a stubby firecracker, complete with a fuse of small-diameter match. Traditionally, these shots are filled with a "dark report" mixture of potassium chlorate with antimony sulfide or sulfur, very similar to the powder in the old-time cannon crackers. It is of course much more powerful than black powder, and requires less confinement, yet in the thin shot casings, it is not so violent as to shatter the comets into dust. Today, flash powder is commonly used in crossettes, and it is practically the only choice in countries such as Great Britain where chlorate/sulfur mixtures are forbidden. There is also a tendency to dispense with the shot casing, charging the flash powder directly into the cavity – which may be formed with a tiny "fuse hole" or "flash hole" at the bottom. Because the powder is practically unconfined once the bottom of the chamber has burned away, this method requires careful adjustment. A slight variation in materials may result in erratic timing or weak bursts. The shotless method is most suitable for large-scale commercial production where the time savings become significant, and where thousands of crossettes can be made from the same batch of materials once their performance has been standardized. Another disadvantage of flash powder is that the bright light detracts from the comet tails, especially the soft gold of charcoal and lampblack. Some hobbyists who refuse to use chlorate with sulfur have broken crossettes with a variety of exotic materials, such as co-precipitates of potassium ferricyanide with a chlorate or perchlorate oxidizer. However, if such methods are used at all in manufacture, it must be to a very limited extent. Very large crossettes with bigger cavities may be split nicely with shots made from commercial black powder. In a good crossette shell, the comets should burn long enough to achieve a wide spread, and then split as nearly simultaneously as possible. Premature cracking spoils the surprise, and if there are many stragglers, this also detracts from the æsthetic value of the shell.

Table 15-20. Silver Stars.

	1	2	3	4	5
Potassium chlorate	59	50	-	-	-
Potassium perchlorate	-	-	32	30	58.5
Potassium nitrate	-	8	-	27	-
FFFFA black powder	-	-	28	-	-
Aluminum, dark (U.S. Aluminum #809)	-	-	6	15	15
Aluminum, bright (U.S. Aluminum 808)	26	21	21	-	15
Aluminum, flitters (U.S. Aluminum #813)	-	8	5	-	-
Aluminum, atomized (Reynolds #120)	-	-	-	15	-
Red gum	7.5	5	-	8	7
Dextrin	7.5	8	8	5	4.5

NOTES: Brilliant silver tailed effects can be produced by the combustion of powdered aluminum at the higher temperatures possible using potassium chlorate (Formulæ 1 and 2) or potassium perchlorate (Formulæ 3, 4, and 5), but the mixtures are difficult to consolidate. Formula 1 relies on a relatively high percentage of dextrin. Formula 2, with flitters, employs dextrin but is also intended to be dampened using thin wheat paste, rendering the composition easier to make into cut stars. Because of the chlorate oxidizer, one should never use paste which has "soured" and become acidic, nor homemade paste which contains alum. Formula 3, with the inclusion of grain powder, is especially adapted for large pumped stars (comets) and is of a type popular in Europe. Formulæ 4 and 5 are rendered denser by the use of dark aluminum for half of the aluminum content, aided in Formula 4 by the use of atomized aluminum, also dense. Formula 5 is intended to be dampened with a solution of gum arabic.

Consistent timing is also important in Roman candles, and will even enhance the effect of mortar-fired crossettes, especially if many are fired at the same time. Uniform mixing, water content and pumping pressure, plus skillful and careful management of the explosive component, are necessary for the best results, and neglect of any of these variables usually shows in the finished product. Some compositions simply do not press as well as others, and any internal cracks, whether they occur during ramming or hasty drying, will ruin the comets. Although crossettes are listed by many makers of display fireworks, truly first-rate ones are not easy to buy.

The term crossettes is taken directly from the Italian *crucetti*, both words suggesting that these comets make "little crosses." When a crossette rises straight up out of a mortar and some of the fragments break outward at nearly right angles, the spark trails may indeed resemble a cross. Also, when a crossette shell performs, many of the streaming fragments will cross each other's paths. The result looks much like a spiderweb, although the actual term "spiderweb" is applied to a different kind of shell. In recent years, a few authors seem to have drawn exaggerated conclusions from the root word *cross*, suggesting for example that crossettes are supposed to break into four even pieces. While this goal may be desirable in some applications, it is not mentioned in older references, nor do the Italian master shell builders, who kept the crossette alive in the United States, seem overly concerned about it. It *is* desirable to have reasonably even breaks, which are neither so weak that the fragments barely change direction nor so strong that the comet disappears in a ball of sparks. We might even say that a crossette ought to break into at least three pieces and no more than eight or ten. The emphasis on four pieces is encouraged by one tool maker's sale of crossette pumps that make a cruciform cavity (Photo 15-15, second from right). Considering the difficulty in adjusting shotless crossettes of any kind, the pre-determined fracture lines are not a bad idea, and these tools sell well. However, most accomplished crossette makers are happy if their comets break smartly at the same time, without shattering into star dust. If for some reason it is deemed essential to have four pieces, there is already a more positive means of achieving this, namely the use of "quadrant comets" which are actually pumped in four pieces (Photo 15-18). The pieces leave a central cavity when assembled, and this is filled with a bursting charge or shot. Each set of four quarters may be assembled on top of a short solid comet, or the quadrant set may be fitted with a time fuse, in which case it is technically a special kind of shell or pupadelle rather than a comet. It is hardly necessary to state that making such devices is extremely laborious, even when compared with other types of specialized comets. When they are used at all, it is in very large cylinder shells which may take dozens or even hundreds of hours to construct. Such shells may be seen at special exhibitions in Italy. Apparently when all the inserts are properly made and timed, they can produce a pattern which closely resembles a checkerboard in the sky.

Comets can be made with much larger cavities than those in crossettes; they may contain flash powder charges to produce loud reports, or very large comets may have black powder burst mixed with smaller stars. Most commonly, the

Table 15-21. Tremalon (flitter, glitter) Stars.

	1	2	3	4	5	6	7	8
Meal D	61.5	68	-	-	-	62.5	-	-
Potassium nitrate	-	-	49	38	48	-	40	51
Barium nitrate	-	-	-	14	9.5	-	14	-
Charcoal, air float	-	-	10	9.5	11	-	10	19
Sulfur	-	-	6.5	14	16	-	11	-
Antimony sulfide	15.5	17	12.5	8.5	-	12.5	-	12
Sodium oxalate	11	-	4	-	-	9	-	-
Strontium carbonate	-	-	4	-	-	-	-	-
Barium carbonate	-	-	-	-	-	-	2	5
Red iron oxide	-	-	-	-	-	-	7	-
Aluminum, bright (U.S. Aluminum #808)	4	5	-	-	-	-	-	-
Aluminum, dark (U.S. Aluminum #809)	4	-	-	-	-	-	-	-
Aluminum, flitters (U.S. Aluminum #813)	-	5	-	2	-	-	-	-
Aluminum, atomized (Reynolds #120)	-	-	8	8.5	-	-	12	8
Aluminum, granular atomized (Reynolds #40)	-	-	-	-	9.5	-	-	-
Magnalium, 50:50, 100-mesh	-	-	-	-	-	9	-	-
Dextrin	4	5	6	5.5	6	7	4	5

NOTES: Formula 1 represents the traditional approach to a gold tremalon, using flake-type aluminums. Mixtures of this type are prone to heating and giving off hydrogen sulfide gas when dampened, particularly when made suitably wet to cut. This tendency is forestalled by using a 1% solution of boric acid in water to dampen it; it is much more efficient to dissolve the boric acid in the dampening water than to include it in the dry mixture. Formula 2 is an analogous white composition, best suited to pumping large (1" and larger) pumped stars or comets. Formulæ 3 and 4 are respectively gold and white effects employing atomized aluminums. Formula 3 is equally good as a cut or pumped star, while Formula 4 is intended as a cut star. Formula 5 illustrates that the effect may be achieved without antimony sulfide. Formula 6 shows the use of magnalium in a variation of the effect. Formulæ 7 and 8 are compositions published by Winokur[25b]. They exemplify the wide variety of compositions that may be used to obtain results generally categorized as 'glitter.'

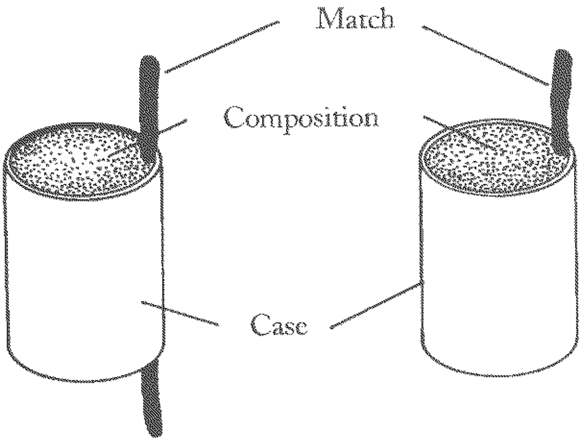

Figure 15-3. Two varieties of pillbox star (after Fulcanelli[86])

cavities are used for secondary color effects which contrast with the comet tails. As a rule, the holes are filled with a "dough" like that used to make cut stars, and allowed to dry thoroughly before finishing. Lancaster[139] mentions the use of a cavity which is just the right size to admit a smaller pumped star, already dry. Comets of this type are not as difficult to make as crossettes, but are still time-consuming because they are pastewrapped in the same way. Many times, the secondary effect is a bright one containing a high percentage of aluminum or magnesium; the difficult ignition which is often a problem with these compositions is easily overcome when they are surrounded by a blazing comet star. Cavity or transformation comets tend to have long burning times, and are seen primarily in Class B Roman candles and large ærial shells.

Pillbox stars, sometimes called simply "box stars," are unique in that they are formed in small paper casings. The name recalls a time when medications were dispensed in round pasteboard boxes, and when true pills (as opposed to tablets or capsules) were commonly made. "Boxes" folded shut on one end have been used, especially for color-changing stars. English pyrotechnists were once fond of "driven" stars, made with dry or nearly dry composition. To make this type of pillbox the thin casing had to be placed in a mould to keep it from splitting; then it could be rammed full of composition like a fountain or serpent. Besides being laborious, this process was quite hazardous with chlorate/sulfur mixtures, and it is rarely if ever used today. The most common type of pillbox star, if any of them can be called common, is open at both ends and is filled with damp composition. The casing typically consists of nothing but a few turns of pasted kraft paper; spiral wound tubes with walls of about 1/16" also give good results. The length is usually a little greater than the diameter; for example, a 7/8" pillbox might be 1" or 1¼" long. A piece of bare match, long enough to protrude about ½" past each end of the casing, must be held in place while the composition is pressed in, either with the worker's fingers or a simple rammer. When large pillboxes are

Table 15-22. Firefly Stars.

	1	2	3	4
Potassium nitrate	49	45	45	38.5
Sulfur	6.5	4.5	4.5	6
Charcoal, air float	29	-	-	45
Charcoal, 80-mesh	11	-	-	-
Charcoal, pine	-	40	40	-
Aluminum, 18-30 mesh flitters	4.5	4	4	2
Titanium, 20-40 mesh flake	-	-	-	4.5
Barium sulfate	-	6.5	-	-
Strontium sulfate	-	-	6.5	-
Dextrin	-	-	-	4

NOTES: The effect of these stars, to which Shimizu[218] applied the name 'firefly,' is to burn with an initial charcoal spark tail, which then appears to transform to a bright metal spark tail. Formula 1 is the composition as originally devised by Jerry Taylor, while Formulæ 2 and 3[218] exhibit the use of barium and strontium sulfates respectively, to enhance the effect as suggested by Shimizu. Formula 4 demonstrates the use of titanium in a manner similar to that of aluminum in the other compositions. Success of the effect depends upon carefully sieving aluminum flitters to eliminate any particles smaller than 30 mesh, which would burn too quickly and thus spoil the transformation. Formulæ 1, 2 and 3 are dampened with thin wheat paste to make cut stars. Formula 4 is dampened with water.

made specifically for cylinder shells, some of them have match protruding from one end only, for a flush fit against the end discs of the shells (Fig. 15-3). It will be seen that pillbox stars bear a strong resemblance to torches; in fact sometimes the compositions are interchangeable. The technique is useful with many compositions which are difficult to ignite, as well as those which are difficult to consolidate as cut or rolled stars. Traditionally, pillbox compositions are chosen with bright, deep colors in mind, and they are often slower burning than compositions used for other types of stars. They frequently contain a slight excess of oxidizer to help burn away the paper casings. For all these reasons, old compositions intended for pillboxes often prove difficult when people attempt to use them for other types of stars. Pillbox stars are almost a thing of the past, as far as commercial manufacturers in the United States are concerned. However, they are still seen in exhibition and competition shells.

Spherical stars are the kind which is meant when the simple term *round* stars is used. Sometimes they are called "rolled stars" after the process used to make them. This form of star is especially associated with the Japanese, and has become almost universal in Asian production. It is only in recent years that round stars have been adopted by Western pyrotechnists. Round stars are "grown" by causing successive layers of composition to adhere to some type of core. In Japan, rounded sand grains of 0.25-0.5mm diameter are commonly used as cores; other starting materials include tiny cut stars, ceramic or plastic beads, birdshot, "peppercorn" pasta, and many varieties of small round seeds such as mustard or rape seeds. Small droplets of water are sometimes allowed to fall into a bowl of composition, causing it to agglomerate into tiny balls or beads which are later enlarged. A common kitchen measuring cup full of cores is sufficient to produce a full batch of stars.

Whatever type of core is chosen, the process is basically the same. Round stars may be made by hand in a round bowl, as described by Shimizu[216], but in industrial production a rolling machine (little more than a cement mixer rotating a highly polished drum or bowl) is typically employed (Photo 15-19). A quantity of cores is loaded into the bowl and an amount of water added. As with much firework technique, a "knack" that is only acquired with experience enables the worker to determine the volume of water to use. A sprayer or atomizer is often used, especially at this initial stage. The grains tumble and are dampened all over with the water; small amounts of the desired composition are added incrementally until the grains pick up the composition and a smooth coating is produced. This is the most difficult part of the process, because the cores are small and light in weight, tending to stick together in clumps. During this stage, very light hand pressure may be exerted on them as they tumble over each other in the bowl, to keep them separate. The same procedure of dampening with water and sprinkling with composition is repeated a few times, until the grains tend to stick together less. In common manufacturing practice it is usual to grow small stars of all the appropriate (*i.e.*, terminal) compositions. These are held as stock from which all the desired sizes and color change combinations are grown as needed.

Table 15-23. Crackling Stars.

	Granules		Matrix	Star
	1	2	3	4
Lead tetroxide (red lead, Pb_3O_4)	89	-	-	-
Bismuth trioxide	-	75	-	-
Magnalium, 50:50, 60 mesh	11	15	-	-
Black copper oxide	-	10	-	-
Potassium nitrate	-	-	51.5	-
Charcoal, air float	-	-	33	-
Sulfur	-	-	6.5	-
Aluminum, flitters (U.S. Aluminum #813)	-	-	3	-
Dextrin	-	-	6	-
Matrix composition	-	-	-	80
Crackle granules	-	-	-	20

NOTES: The crackle effect is produced by granules or micro-stars of a crackle composition heterogeneously mixed with a nitrate-charcoal matrix composition and formed into stars. Formula 1[219] or Formula 2[121] are mixed with a 10% solution of nitrocellulose in acetone or amyl acetate to form a dough, and made into small cut stars, then broken apart. What is retained on 18-mesh and passed by 8-mesh is retained for use. To 100 parts of the matrix composition, Formula 3, is added 25 parts of the granules, resulting in an 80:20 matrix/granule mixture, Formula 4. This is then dampened with water sufficiently to form pumped stars.

Two distinct techniques are used for growing stars beyond the initial coatings of the core. In the West, the entire star is most often grown by the process of alternative dampening with water (or other solvents) and addition of dry composition. In Japan, there is a particular technique in which a thin, fluid, paste (*toro*), made from the composition mixed with water, is used to dampen the stars between additions of dry composition. The properties of glutinous rice starch as a binder are especially well suited to this method. Whatever technique is used, attempting to grow stars too rapidly is likely to make them irregular in size, cause cracking or flaking, and cause problems in drying. Shimizu has used the term "driven in" to denote the drying of the outer surface of the star forming a hard "shell" inside which moisture from incompletely-dried inner layers is trapped. This renders the stars next to useless. The growth increment is best kept quite small, with frequent intervals for drying. Care should be taken with the small stars if they are dried in the sun; they will be more sensitive to friction, etc., but will also be much more porous than cool stars. It is good to let them cool down before handling or any further coating is done. The stars are grown with the first composition (*i.e.*, the last composition to be observed when the star is burning) until the desired diameter is achieved, and they are dried.

The rolling method is the most efficient way to make color-changing stars, which are used in many elaborate and beautiful shells. Making these stars can become quite complicated, but a few general guidelines are worth mentioning here. The final effect of a color-changing star is often a brilliant one containing metal fuel, which helps to compensate for the smaller size of the star at this stage. While normal color compositions do not typically have notable differences in burning temperatures or characteristics, and hence have no difficulty transferring fire, such compositions as the barium nitrate-based *koro* (Formula 3, Table 15-25), or some types of strobe compositions, will not reliably ignite directly from an adjacent cool-burning composition while moving through the air. The usual Western solution for this is to use an intermediate priming layer of "hot prime," often containing silicon or a metal powder, or a mixed ignition layer in which a blend of the two compositions is present. In the Japanese technique, the change is easily accomplished by using the *toro* of the inner layer to dampen the stars, then adding the dry composition of the outer or succeeding layer. This is done a couple of times before a *toro* is made from the outer layer's composition, from which point this is used to dampen the growing stars through the completion of that layer. If the desired effect is from a charcoal (*i.e.*, cool burning) to a flash or silver (*i.e.*, with a high ignition temperature), then an intermediate layer of prime is used for a couple of coats: thus the charcoal easily ignites a thin color-style coat which easily ignites the metal-containing composition.

One consideration with which it is necessary to deal is the danger of mixing incompatible compositions at the transition point between layers. Compositions containing ammonium perchlorate must be separated from those containing nitrates or chlorates, for reasons of hygroscopicity and safety. Of a slightly different sort of concern is the mixture or contact of chlorates with sulfur. Such mixtures are almost unanimously considered best avoided, and this can be

Table 15-24. Round Stars (colors).

	1	2	3	4	5
Potassium chlorate	57	60	60	65	45
Black copper oxide	7	-	-	7	-
Strontium carbonate	7	17	-	-	-
Barium nitrate	-	-	-	-	30
Cryolite	-	-	16	-	-
Red gum	10	6	9	10	10
Rosin	-	3	-	-	-
Magnalium, 50:50, 200 mesh	5	-	2	-	-
Chlorinated rubber	10	-	-	13	5
Hemp charcoal	-	10	8	-	6
Dextrin	4	4	5	5	4

NOTES: While many of the star compositions listed under other headings may perform satisfactorily as round stars, these compositions are specifically adapted for such use, and are representative of those used in Japan for the purpose. Formula 1 is purple (*murasaki*); Formula 2, red (*beni*); Formula 3, yellow (*ogon*); Formula 4, blue (*ao*); and Formula 5, green (*midori*). In formulating colors for use in *warimono*-type shells, not only must good depth and brightness be sought, but also burning speed, so that colors change with the regularity and rapidity necessary for the perfect firework 'flower,' and the burst does not appear to droop, a serious æsthetic flaw.

accomplished easily enough by using perchlorates as oxidizers, though they have their own defects and the dangers of perchlorate/sulfur mixtures are themselves not always insignificant. However, it is worth evaluating carefully and thoughtfully the dangers involved when chlorates are used, since the advantages of using them in stars for round shells should be apparent.*

If the layers might combine to form, say, ammonium chlorate, then another plan must be made, but if the result will be a mixture of chlorate and sulfur together with phlegmatizers and acid-neutralizers (*e.g.*, strontium carbonate), the concern should not be so great: although such mixtures are sometimes frighteningly sensitive to friction, that factor has no play in a finished, densely-consolidated star, in which the dangerous admixture is buried well below the surface and is, itself, not subject to friction. In any event, as with all published pyrotechnic knowledge, the reader must himself assess the level of risk he is competent to handle, the only acceptable alternative to which is not using any of this information in practice, at all.

Even when compatibility is not a problem, a thin layer of "changing relay" (*e.g.*, Formula 4, Table 15-16) may be used between color layers, especially in stars for large, fancy, chrysanthemum shells. The relay composition burns very dimly and it is argued that this makes the transition between colors appear sharper and cleaner. To make stars with three or four color changes the worker might have to change compositions ten times, and then grade, and sort, the growing stars by size several times. In practice this is very rarely done; for carefully made stars having a simple transition, *e.g.*, brocade to blue, perform beautifully in the sky without need for such complications.

Aside from use in color-changing effects, there are some compositions which simply perform better when made into round stars, probably because they attain greater density from rolling than they would have if made into cut stars. This is especially noteworthy in willow compositions which contain very high percentages of charcoal. When metal powders are added to these already fuel-rich compositions, the final product may contain as little as 25% potassium nitrate, amongst the lowest oxidizer contents of all the mixtures used in display fireworks (Table 15-25, Formula 6). Yet correctly made stars burn smoothly as they travel through the air at high velocity. Ferro-titanium has become a common ingredient in round stars, not only for willows but in the fast-burning chrysanthemum effects as well (because this alloy has hard gritty particles, it is best avoided in star pumps, and it can be troublesome in cut stars also). Ferro-titanium produces a bright golden tail, and it can be added to a regular willow effect to produce a fast – almost glittering – firefly effect, known as "brocade willow" or *nishiki kamuro*. Similarly, it can be added to a faster-burning pine coal star to give *ginpa* or "golden wave." A different composition is used to produce the brocade effect for

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* In case they are not, a few are mentioned: good colors with large flames are produced, while ignitability, ferocity of burning, and speed of burning are all high. These last issues are of paramount importance to the correct operation of chrysanthemum shells, which are very hard breaking, and of short duration as compared with most Italian-American shells.

Table 15-25. Round Stars (tailed and bright effects).

	1	2	3	4	5	6
Potassium nitrate	50	-	-	56	35	29
Potassium perchlorate	-	50	13	6	-	-
Barium nitrate	-	-	44	-	-	-
Hemp charcoal	10	2.5	-	11	-	-
Pine charcoal	-	-	-	-	45	34
Red gum	-	2.5	-	-	-	-
Sulfur	12	-	9	-	11	6
Antimony sulfide	10	-	13	6	-	-
Magnalium, 50:50, 100 mesh	14	-	-	-	-	-
Aluminum, bright (Reade #100)	-	-	-	17	-	-
Aluminum, mixed	-	35	-	-	-	-
Aluminum, dark (German black)	-	-	18	-	-	-
Ferro-titanium, mixed	-	-	-	-	-	25
Dextrin	4	-	3	4	-	-
Soluble glutinous rice starch	-	10	-	-	9	6

NOTES: Formula 1, twinkling (*kirakira*), Formula 2, silver (*shiragiku*), and Formula 4, brocade (*nishiki*), are fast-burning compositions typically used in *warimono*-type shells. Formula 3, silver flash core (*koro*) is often the final color change of a color-changing star. Formula 5, willow (*kamuro*) and Formula 6, brocade willow (*nishiki kamuro*), are long-burning stars with considerable excess fuel, used in willow and diadem shells.

a peony shell (*nishiki botan*), and this is usually a cool-burning aluminum mixture (Table 15-25, Formula 4).

The stars are all similarly finished with a thin layer of a pine charcoal tail composition, followed by another layer of a basic priming composition similar to black powder. The effect of this universal finishing is observed clearly in a shell's performance: the points of light from the stars do not originate at the center of the burst, but rather a small radius away from it. The effect is cleaner than would otherwise be produced, as the small distance the stars have traveled by this stage helps even out their speeds so that the appearance of good symmetry is produced. Also – again, from an æsthetic point of view – the flower is seen to "click on" rather than develop from a small point; this is considerably more elegant than the stated alternative.

The ability to turn out large numbers of color-changing stars is the greatest attraction of the rolling method. However, it often has another advantage which becomes apparent in factory scale work. Naturally, once the composition is prepared and dampened, it takes about twice as long to cut twenty pounds of 1/4" cubic stars as it does to cut ten pounds. But once the cores are properly started, it does not take any longer to roll a thousand round stars than it does to roll five hundred, and with equipment of suitable size, increasing the batch to 10,000 only increases the production time a little. If, for example, a large batch of 1/4" red stars is made, part of them can be primed and dried at that size, while others go on to become 3/8" red stars, or 1/2" color-changing stars. The small, irregular pieces which pass the 1/4" sieve are likely to be used in consumer fireworks.

In Japan and China, it has long been the rule to use round stars in practically everything, from small single-color shells to rockets and mines. More recently, manufacturers in many Western countries have taken advantage of the mass-production potential of round stars, and have added a twist of their own. Today it is not unusual to find American-made cylinder shells with round stars. Some compositions, particularly when they contain ingredients of widely divergent densities, or those not mixing well with water, do not roll well, especially as the stars become larger; 3/4" zinc or lampblack streamers can be made more quickly and with less frustration by cutting them. With ordinary sizes and types of stars, good quality can be achieved by the mechanized rolling process. Although many compositions will roll well, some specially suited to this method are given in Tables 15-24 and 15-25. Further information on round stars may be found in works by Bleser[18], Clayre[36], and Shimizu[216].

A note is made here in passing about the "crackle core." This is an older effect differing from that described above and in Table 15-23. This core is similar in effect and even in design to the "cracker ball" previously described under the heading of exploding fireworks. A composition of arsenic disulfide (realgar), potassium chlorate, and starch is dampened and painted onto a good quality tissue paper just as in the Japanese technique of making "powder pasted paper." Once this is *almost* dry, it is rolled up and the roll tightened by repeated rolling under gentle pressure, as in case rolling.

Table 15-26. Dark Report Compositions.

	1	2	3	4	5
Potassium chlorate	50	66	54	64	-
Potassium perchlorate	-	-	-	-	69
Antimony sulfide	50	17	31	27	-
Sulfur	-	17	-	-	-
Potassium ferricyanide	-	-	-	-	31
Rosin	-	-	15	-	-
Asphaltum	-	-	-	9	-

NOTES: Formulæ 1 through 4 are representative of the type of 'fulminating' composition once generally used for noise in fireworks and illustrate the basically uncritical proportions and combinations of ingredients. They are needlessly sensitive for this purpose and are generally now reserved for those few uses in which noise or explosive force without a high light output is needed, as, *e.g.*, in a crossette shot, or in the echo reports of a hammer shell. Formulæ 3 and 4 include organic fuels intended to produce smoke that will further obscure the already dim light produced. Formula 5, from a patent by Fronabarger[85], is prepared by co-precipitation. The components are dissolved in as small an amount of hot water as possible, then the solution poured into an excess of chilled isopropanol. The supernatant liquid is decanted from the co-precipitate, and the latter granulated and dried. Such compositions can be very brisant and may be of use in jurisdictions where the traditional chlorate/antimony types are forbidden by regulation.

While still damp, the roll is cut up into short lengths corresponding to the roll's width. These are used as cores, being immediately coated with a safe composition and left to dry. Once dry, the dangerous mixture is already under a coat of a more ordinary composition, and the cores are relatively safe to handle. They are then built up to the desired diameter as in usual practice.

The stars burn singly as a normal star, but end with a sharp snap. Crackle cores are normally used at the center of color or willow stars, and the shells made with these stars perform as usual, only to end in a searing wave of high-pitched cracks; this effect is quite unlike the continuous crackle produced by the earlier-referenced lead or bismuth oxide/magnalium granules embedded in a gunpowder-type matrix.

Almost every step of the manufacture of Japanese-style crackle-core stars represents a danger level above and beyond the norm: mixing the ingredients, having tools and work surfaces on which the drying mixture may be present, rolling the paper, coating the cores, and subsequently drying the stars. This makes these articles a specialty for the few manufacturers willing to stand the risk, and they have a ready market amongst the much larger number of pyrotechnists who are not. This information is provided as a description only, with the warning that experimentation with these stars is ill advised.

Besides the countless varieties of stars and comets, many other payloads or *garnitures* can be used in ærial devices. Most of these inserts have paper casings, and bear a resemblance to the corresponding ground fireworks.

Exploding inserts are used in all styles of firework making, and they exist in great variety. Occasionally they are still made with black powder, or with "dark report" compositions containing potassium chlorate, especially when it is desirable to avoid a bright flash which would detract from delicate color effects. Dark report mixtures are not completely flashless, but do produce very little light; some of them are designed to produce extra smoke which obscures the already dim flashes (Table 15-26). For special exhibition fireworks, principally in Malta and southern Italy, colored flash powders are sometimes made (Table 15-28). Some of the aforementioned mixtures require strong, carefully constructed casings in order to produce a loud noise. However, the vast majority of units are made with aluminum flash powders which need relatively little confinement (Table 15-27). With these powders, the most important aspect of the casing design is that it must be able to withstand the force of the propelling or bursting charge. Salute shells, bottom shots and timed shots, indeed all explosive inserts which exceed 1¼" to 1½" diameter, are usually made with thick-walled casings and reinforced with string before being pastewrapped. They are, in fact, cylindrical shells and their construction will be explored under that heading. For smaller explosive components, the casings can be surprisingly thin as long as they are tough and well sealed. Such construction minimizes the amount of dead weight a rocket or shell has to carry. Even more importantly, avoiding the use of plaster, hard-pressed clay, or brittle plastics eliminates hard debris which could injure bystanders in the event of a low burst.

Table 15-27. Flash Report Compositions.

	1	2	3	4	5	6	7
Potassium chlorate	62	-	-	-	-	-	-
Potassium perchlorate	-	67	67	70	-	30	45
Potassium dichromate	-	-	-	-	-	-	5
Barium nitrate	-	-	-	-	57	30	-
Aluminum, dark (U.S. Aluminum #809)	23	25	12.5	-	-	20	-
Aluminum, dark (German black)	-	-	12.5	30	29	-	-
Aluminum, atomized (Reynolds #200)	-	-	-	-	-	20	-
Magnesium, 120-300 mesh cut	-	-	-	-	-	-	50
Sulfur	15	8	-	-	14	-	-
Antimony sulfide	-	-	8	-	-	-	-

NOTES: Formula 1, with potassium chlorate, is typical of compositions once widely used in the United States (though forbidden by regulation in many other jurisdictions). Formula 2 is more typical of present-day American practice. Formula 3 employs German black aluminum and antimony sulfide to increase charge density and 'sharpen' the noise. Formula 4 is perhaps as safe as a flash powder can be, and with the proper aluminum, makes a very satisfactory explosion. Formula 5, with barium nitrate, is dense and functions well with suitable confinement. Formula 6 is formulated for light output rather than noise, though it yields a loud report in a typical salute. Formula 7[230] is untypical in modern display work in that it contains magnesium. The potassium perchlorate and potassium dichromate are ball-milled together, then blended with the metal. Such compositions make exceedingly bright flashes and loud noise in relatively small quantities, and call for even greater caution in handling than other flash powders.

Table 15-28. Colored Flash Compositions.

	Red	Green	Yellow
Potassium perchlorate	54	-	-
Potassium chlorate	-	-	46
Barium chlorate	-	50	-
Strontium oxalate	11.5	-	-
Strontium carbonate	11.5	-	-
Cryolite	-	-	16
Aluminum, dark (German black)	-	25	23
Magnesium, 120-300 mesh cut	15	-	-
Antimony sulfide	-	12.5	10
Sulfur	-	12.5	5
Red gum	8	-	-

NOTES: These traditional compositions for colored salutes require handling with great caution.

Spectators often assume the flash reports they see in ærial displays are made with magnesium, but this is rarely the case. Magnesium powder is more expensive than aluminum and it is much more susceptible to corrosion; therefore it has to be treated with an inhibitor if the items made from it are to be stored for a significant length of time. Fine granular magnesium can produce very violent flash powders which will make a bang if a few grams are burned in a loose pile, yet for maximum performance in salutes, these powders may require stronger casings than their aluminum counterparts. Another paradox is that while magnesium flash powder generates more energy per unit mass than the usual aluminum mixtures, it is also bulkier; the decreased loading density often means that a magnesium report is not as loud as an aluminum report of the same size. Despite these drawbacks, magnesium flash powders are sometimes seen in exhibition work where exceptionally bright flashes are desired. Magnalium is also used to a limited extent.

As might be expected with something so widely used and potentially hazardous, aluminum flash powders inspire a certain amount of controversy among firework makers. Chlorate flash compositions are sometimes claimed to be too sensitive for use in shells. Actually, they were used extensively in the past with a fairly good safety record, and are still used in some countries, even in massive cylinder shells of eight, ten, and twelve inch caliber which undergo more stress on firing than normal commercial shells. Salute shells made with *any* type of flash powder can explode in the mortars with devastating results, but this can usually be traced to defects in the shell casing rather than the composition. Still, chlorate flash powders are significantly more sensitive to shock, especially if they also contain sulfur or antimony sulfide; accidents in processing being of more potential concern than those in the performance of finished devices. They are a legacy of the days when perchlorate was less available, and when most of

Table 15-29. Rosette, Titanium Report, and *Hanarai* Compositions.

	1	2	3	4
Potassium chlorate	44	52	-	-
Potassium perchlorate	-	-	55	35
Aluminum, bright (U.S. Aluminum #808)	44	26	-	-
Aluminum, dark (U.S. Aluminum #809)	-	-	28	-
Aluminum, fine stamped (P-1000)	-	-	-	10
Antimony sulfide	12	16	7	5
Titanium, 20-40 mesh sponge	-	-	10	-
Ferro-titanium, mixed	-	-	-	50
Dextrin	-	6	-	-

NOTES: The 'rosette' effect is made with granulated chlorate flash. Formula 1 is dampened with wheat paste, Formula 2 with water, until the mixture is a coherent doughy mass; the composition is then granulated through 3 × 3 or 2 × 2 hardware cloth, dried, and loaded into light cases. The effect has largely been superseded by the use of ordinary flash powder to which coarse titanium has been added, as in Formula 3. This requires the use of conventional report casings. Zirconium has also been used for spark production in fireworks by a few experimenters; the effect is similar to that of titanium but a brighter and "cleaner" white. In the absence of information to the contrary, such mixtures should be considered even more hazardous than the analogous titanium compositions. Inclusion of antimony sulfide in zirconium flash powders is probably inadvisable. Formula 4 represents the Japanese counterpart of the titanium report, called *hanarai*. Note the comparatively large percentage of ferro-titanium.

the aluminum powders were heavily coated "bright" flakes. With the more reactive pyro grades, there is little discernible difference in the performance of chlorate and perchlorate flash powders, except in the smallest devices. While chlorates may be used safely enough in most colored stars, the added safety margin is normally reason enough to favor potassium perchlorate for reports. There are many brands of "pyro" aluminum, and while some pyrotechnists have a favorite, any of them will give good results in mixtures of this type. The German dark pyro is the most reactive and has the added advantage of being denser than the others, but has become prohibitively expensive for some applications. American pyro aluminums such as United States Aluminum #809 cost much less and are not far behind in performance, especially as the size of the reports increases.* Some pyrotechnists will use only binary mixtures of perchlorate and aluminum; others equally experienced feel there is no significant increase in the hazard when they add sulfur, to make the reaction products gassier and produce a more forceful, low-pitched boom.

In the interest of greater safety, many people have advocated nitrate oxidizers in flash powder. In these mixtures, the grade of aluminum becomes more important, and sulfur is practically always added to make the powder more ignitable. Barium nitrate flash powder has a high density, and can produce a good sound level in large bottom shots. However, in the ubiquitous three-inch salute, it is noticeably underpowered when compared with its perchlorate rivals.

In the United States, the National Fire Protection Association (N.F.P.A.) has promulgated its standard 1123-2000, which allows maximum sizes of 5" in diameter and 5" in height for single-fire salutes (with no weight restriction), and 3" in diameter with a 3-ounce flash powder limit for exploding components in multiple-break or multiple-effect shells. Many people, including some who sell display fireworks, falsely believe that larger reports are "illegal," when in fact, the N.F.P.A. has no statutory regulatory authority. However, since most display operators are legally obligated to buy insurance, and most insurance underwriters require adherence to N.F.P.A. guidelines, large salutes are rarely stocked by wholesalers. Undoubtedly, this has discouraged the already limited use of nitrate flash powders. In practice, potassium perchlorate and pyro aluminum, with or without sulfur or antimony sulfide, works very well in devices ranging from the smallest shell inserts to the largest bottom shots.

Mixing flash powders can be another area of contention. Some makers pass them through sieves as they would most other compositions, being very careful to throw any coarse particles away rather than try to force them through the screen. Others find that there is no performance gain which would justify the mess and danger of sieving. They like to sieve the oxidizer alone, or perhaps with sulfur or antimony sulfide, to break up any lumps. After the aluminum is added, final mixing can be done on a sheet of paper with a soft brush or in a paper bag. Some factories accomplish this final step with a cylinder or a V-shaped combination of cylinders, which can be slowly revolved in a barricaded area by machine.

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* Atomized aluminum is hardly ever used in flash powder for fireworks, due to its difficult ignition and slower burning rate.

In all cases, methods and materials which generate static charges must be avoided, and it is wise never to mix flash powder on days with low humidity, especially in the wintertime. Ball milling and other methods which create friction are never a wise idea with flash compositions. Titanium has been a popular ingredient since the 1970s; it increases the friction hazard and should always be added last, especially if the powder is sieved (*e.g.*, Formula 3, Table 15-29).

As with exploding ground fireworks, many different names are applied to the ærial versions, and some of these can be arbitrary and confusing. The word *salute* is sometimes used as a generic term for any explosive firework, but is really only correct for one which produces a single, loud bang as its only effect. This may be a stout firecracker shot on the ground, or an ærial salute. The term is derived from military usage, where, especially in the Navy, a blank cannon load or an exploding rocket was often used as a greeting to friendly forces.

Report is supposed to mean an explosion which occurs after a color burst or other effects, the idea being that the final loud noise confirms or "reports" that the whole device has finished its performance. In some cases there is more than one report in this final position, *e.g.* "green and silver with five timed reports." A simple explosive heading on a rocket is also legitimately called a report, since the rocket's tail may be considered a separate effect with an æsthetic or signalling value of its own.

The word *shot* is traditionally used in pyrotechny to refer to almost any explosive effect, although it does imply one more powerful than those classified as "crackers." A final explosion in a multibreak cylinder shell is commonly called a *bottom shot*, even when it is not an insert but a separate, full-diameter section. *Timed shots* use carefully prepared fuses to make them explode at evenly spaced intervals, while *fusillading shots* produce a more random, rattling series of blasts often called a *cannonade*. Use of the term "shot" does not imply any specific construction method, and there are many traditional kinds as well as modern variants.

The *saettine*[*] generally has a thin, flexible casing and is fused with bare match to provide a short delay. Such casings are usually rolled with a strip of thin chipboard inside the kraft paper; this not only stiffens the walls but keeps the height consistent. The end is closed with a simple tongue or triangle fold, sometimes brushed with paste or glue. Saettines are typically ¾" to 1" diameter and about two inches long, and are only partly filled with powder. The upper ends (where

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[*] The word (pronounced sī-ă-tēn) is the diminutive of Italian *saetta*, from Latin *sagitta* or arrow. From it, by back-formation, derives the verb *saettare*, "to shoot,"*e.g.*:

"Crudo Amor mi saettò"

[Orsini, *Il Floridoro*]

From this *saetta* came to mean "shot," also figuratively a lightning-bolt or thunder clap:

"Tempra il Ciel le sue saette
per punir chi l'irritò"

[Ansaldi, *San Giovanni Battista*]

Thus *saettine*, a "little thunderclap" or "small shot."

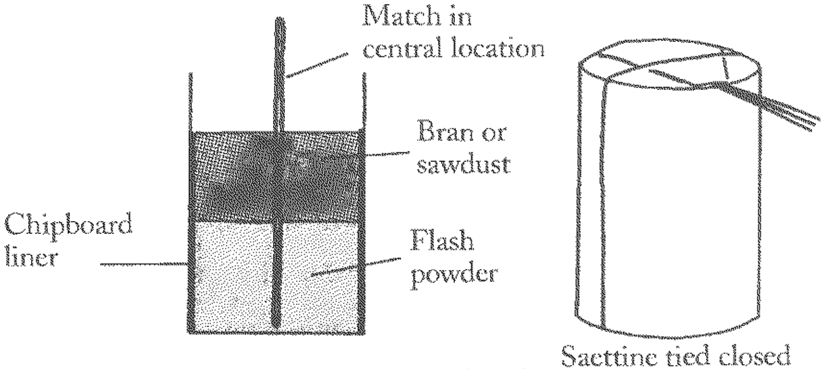


Figure 15-4. Saettines.

the match enters) are filled with compacted sawdust or bran before being folded and tied shut (Fig. 15-4). Saettines are not normally pastewrapped, and even when well made, they feel softer than most other shell inserts. The layers of inert filler protect the powder from the bursting charge of the shell, and also slow the burning rate of the match enough to allow the shots to spread out before they explode. This technique is not as precise as the use of true time fuses, but is much more expedient and less expensive, and good saettines are quite consistent. Some purists in the Italian style of shellbuilding (*q.v.*) have a convention that saettines, like most other shell inserts, should perform in a symmetrical ring, and they avoid using this term for any shots which do not do so. Good ring patterns can be achieved in shells of five-inch and larger caliber, and are a particularly attractive use of titanium saettines. However, there is nothing in the word itself which implies a ring, and this certainly cannot be expected from small shells, or when saettines are fired one at a time from mortars. It is also worth pointing out that saettines were being made with "dark" report compositions long before flash powders were introduced, and without the flashes, it is difficult to tell whether the shots explode in a ring or not, unless the shells are fired in the daytime. Another common method of making shots is to ram clay around bare match and load the powder afterward; this requires heavier casings, and machine-wound tubes are often used. Among many manufacturers, the word "saettine" (with various phonetic spellings) has come to mean almost any kind of fusillading shot, whether plugged with sawdust, clay, or even plastic. Other traditional terms for small shots include *scoppietti* ("little explosions"), *lambetti* ("little lightning flashes") or simply *bombi*. Although these devices are deemed small – which they are in comparison to timed reports or bottom shots – they are at least as powerful as the old cherry bomb and M-80 firecrackers, usually more so. When children are injured playing with duds recovered from professional displays, insert shots are often involved. They appear insignificant, but their fuses are very fast, and each contains several grams of potent flash powder, enough to destroy a hand or an eye.

Japanese *rai* (thunders) are spherical or spheroidal report inserts typically one inch or less in diameter. Two techniques are used for their production. In the older and more laborious one, the explosive mixture is contained in a tissue paper pouch or sack, which is fused, then wrapped with paper strips and bound with string. This technique is still used in special cases where the reports need to be more compact than is possible with the cheaper alternative method employing mechanically produced strawboard hemispheres. In both methods, the timing elements used are prepared by cutting Japanese spun time fuse to length, pasting short tissue paper tubes on one end of each, filling these tubes with fine black powder as a priming charge, and twisting them closed. Likewise, the composition is, in both methods, measured (about a teaspoonful, 5g) onto squares of tissue paper; the four corners are gathered to the center, and twisted off to form pouches. From this point, the method of producing the thunder charges without casings proceeds as described by Clayre[35] (Photo 15-20). If the more common strawboard hemispheres are to be used, the punched hemispheres are fitted with prepared fuses, the ends having the small black powder priming tubes placed inside. The powder pouches are carefully punctured at the bottoms (*i.e.*, the centers of the initial tissue squares), and pushed into the hemispheres onto the primed fuse ends. The surplus twists of tissue are crushed down over the powder pouches, and solid hemispheres placed on top to form complete cases. The assemblies are then taped together at their equators, sealed around the fuses with white glue, and covered with pasted paper in the manner of *poka*-type spherical shells. After drying and priming, they are ready for use. They may be embedded in the bursting charge of a large ball shell, or arrayed around the outside of the case like stars, and usually produce a rapid fusillading effect like that of saettines, though they may also be of different timings for a timed-report effect. *Hanarai* (thunder flowers) have a visual effect, arising from the inclusion of high percentages of ferro-titanium in the composition (Formula 4, Table 15-29). Antimony sulfide is used in this type of flash powder to maximize its burning rate and explosive force, in order to compensate for the high percentage of excess metal. In this case, the increased friction hazard is accepted as a necessity; it ceases to be a problem after the articles are wrapped and tied, or loaded into hemispheres. It is interesting to note that production of *rai* by the method of wrapping with dry paper and binding with string is considered man's work in Japanese factories, while those made from hemisphere sets are usually paste-wrapped by female workers.

In addition to the use of bare match as a delay fuse, another inexpensive and ingenious method can be used to time small explosive shots. It involves a modified slurry priming, which has been especially well developed in Malta. The Maltese are fond of large multibreak noise shells which may contain hundreds of small reports of different sizes, and sometimes different colors. These shots are filled, closed, and wound with a few turns of twine, but are not equipped with any kind of cord fuse. When it comes time to build a shell, the side of each shot is pierced with a specially made awl, and the orifice is primed with black powder paste containing an additive which decreases the burning rate. The makers are rather secretive about their favorite priming mixtures, but suitable retardants include barium nitrate, barium carbonate, and higher than usual levels of gum binders. Successive timings, of course, contain larger and larger percentages of the retardant. The Maltese commonly achieve three or more distinct barrages of reports from one shell break by using this method. It requires considerable skill and experience, but once mastered, it offers several practical advantages. The need to buy machine-made time fuse (which would have to be primed anyway!) is eliminated. Great numbers of shots can be made in advance and stored without committing to a particular timing; the lack of fuses makes them safer and more resistant to handling than most other components. For big cylinder shells, a most important advantage of these *bombi* is that they are sturdy and compact, and fit neatly into layers to make very strong shells.

Rosettes are made with coarsely granulated flash powder containing a high percentage of "bright" flake aluminum (Formulæ 1 and 2, Table 15-29). They explode more softly than other shots, with a "thud" or "splat" rather than a sharp "bang," and a short-lived silvery spray. Rosettes are usually a little larger than saettines, and have a true time fuse instead of bare match. They are normally expected to burst in ring patterns, and there may be more than one timing in a shell break. The effect resembles that of titanium shots, and has become less common since titanium has come into widespread use.

The *lampo muto* or silent flash unit is uncommon in most countries. These devices have thin casings similar to those used for saettines, and need slow, bright flash powders, often made with relatively coarse grades of magnesium. They are difficult to adjust, since they must be sturdy enough to withstand the burst of a rocket or shell, without causing the flash charge to make a significant noise. In Spain, similar devices called *relampagos,* consisting of simple paper "flash bags" tied to pieces of primed time fuse, are fairly popular in rocket headings.

Serpents used in ærial work typically have a burning time of three to five seconds, although they can safely last longer if ignited at high enough altitudes. The same applies to most other tubular shell inserts. Such articles are needed in volume and are customarily gang-loaded with the aid of machinery (Photo 15-21). Great uniformity in performance can be obtained through control of the process. When these items are prepared for shells, rockets, or mines, it is usual to smear slurry priming in and around the chokes and to dredge them in fine grain powder. Often a piece of bare match is also imbedded in the priming, and in this case, the tube may have a paper nosing around the match. Today, black powder compositions with titanium are quite common in tubular garnitures, but plain charcoal types are still seen, as well as some which contain aluminum or ferrotitanium. Serpents may be known by other names; the term "fish" is often applied to ærial types, especially those which are not choked. Most serpents range from 5/16" to 1/2" i.d., but for special applications, they can almost be any size. Brock[26] mentions a favorite type of sixteen-inch shell which contained a hundred 3/4" bore rockets! By the conventions of shell building, these could legitimately be classified as large and powerful serpents, and prepared accordingly.

Whistles used in shells differ little from those fired on the ground, although again it is important to have good control over the burning time. Many whistle compositions are quite sensitive to changes in pressure or overly strong ignition,

Table 15-30. Hummer Compositions.

	1	2	3
Meal D	90	90	-
Potassium perchlorate	-	-	56
Resorcinol resin	-	-	28.5
Paraformaldehyde catalyst	-	-	7
Titanium, 60-100 mesh sponge	10	-	8.5
Ferro-titanium, mixed	-	10	-

NOTES: Formula 1 is for a silver, Formula 2 for a gold effect. These are to be rammed in short, heavy-walled tubes with clay plugs at the ends. Formula 3[71] is the composite-type mixture and gives a silver spray. The perchlorate, the catalyst, and the titanium are mixed dry, then incorporated with the liquid resin and introduced into the pre-drilled and matched tubes like the composition of a pillbox star. Once mixed, the composition has a working time of perhaps one hour. The tube ends are sealed with a vinyl cement.

and will explode if the confinement is too great. For this reason, large blobs of priming are best avoided, and whistles generally work best with bare match which is simply tied into thin paper nosings. Extra-strong bursting methods, such as chlorate mixtures or flash bags, are rarely used in whistle shells for the same reasons. Shell whistles are typically no larger than one-half inch bore, and frequently contain titanium to give them silver tails.

Spinning tube garnitures are very popular and may be divided into two basic categories. Shell *tourbillions* are about the same size as the kind sold to the public (pp. 211-214), but they lack the familiar stick or "wing." They usually have a single vent hole drilled near one of the clay end plugs, although sometimes there is a hole at each end. The hole is drilled at a 90° angle to the bore of the tourbillion, causing it to tumble end over end as though it were a free-ranging saxon. Shell tourbillions have a rather lazy looping flight and are particularly effective when they are deployed in symmetrical rings. The effect suggests a circle of figure skaters or ballroom dancers whirling in unison. *Hummers* are normally shorter in relation to their diameter than tourbillions; a representative size is ½" i.d., 1" o.d. and 1¼" long. The vent hole in a hummer is drilled tangentially, generally at the center of the tube. This causes it to rotate around its longitudinal axis at a very high rate of speed, producing a buzzing noise which suggests bees or hornets. Hummers are usually charged with fast-burning gold or silver compositions which contain high percentages of commercial black powder, although magnalium color mixtures and other exotic types can be used (Table 15-30). No matter how they are arranged in a shell casing, hummers cannot be expected to stay in orderly formations; in fact their random flight is part of their appeal.

Self-propelled color stars called "go-getters" or "shooters" are a relatively recent innovation. Other fast-burning stars, notably pillboxes made with aluminum mixtures, may exhibit a "swimming" movement, but go-getters are specifically designed to enhance this effect. They are filled with magnesium compositions that use plastic binders and acetone or another volatile solvent to speed drying time. Bare match is inserted into each tube while the composition is still gooey. Upon ignition, the match burns away quickly, leaving a cavity like that in a skyrocket. As the enlarged surface of composition burns, it lends a propulsive effect to the article. These devices may be viewed as specialized pillbox stars, or as a kind of colored serpent.

Most tubular garnitures, especially serpents, tourbillions and whistles, can easily be equipped with small charges of flash powder so that they end with reports. As with saettines or scoppietti, the main consideration is to make sure that they do not explode prematurely when the shell bursts. Besides the usual paper plugs, the ends of these devices are often reinforced with hot-melt glue or a mixture of ordinary white glue with sawdust.

Small bombshells containing stars and bursting powder are often inserted in mines, Roman candles and the heads of rockets. However, their most dramatic use is when they are placed inside larger shells, and they are usually simplified miniatures of the parent type. For details of their construction, the reader is referred to the "shell-of-shells" (pp. 222-224 and 233-235).

Comets

The simplest kind of ærial firework consists of a single pumped star, propelled from a mortar tube by a black powder lifting or "blowing" charge. Tailed stars are normally used, and a complete unit (including a disposable paper mortar and its wooden or plastic base) is called simply a "comet." Many different types of comet stars are used, including crossettes and comets fitted with a secondary burst of small colored stars. In some of the older American texts, the term "meteor" was promoted to specify a bright star made with magnesium or aluminum, while the traditional "comet" was reserved for black powder versions. This distinction is not common today. Comets sold to the public rarely exceed 1¼" diameter in the United States, where consumer fireworks guidelines allow a maximum of 40 grams of composition in a single tube item of this class. Spiral-wound mortar tubes are adequate for one shot and have become the standard because they are cheaper than parallel-wound ones. Similar devices, usually more heavily charged, are also used in professional displays. Sizes are quite uniform in the United States, because most companies which manufacture them buy the tubes and bases from the same handful of suppliers. Some of the standard sizes are:

	I.D.	**Length**
#0 Mortar	¾"	3 ½"
#1 Mortar	1"	5"
#2 Mortar	1 ¼"	6"
#3 Mortar	1 ½"	6"
#4 Mortar	1 ¾"	8"
#5 Mortar	2"	9"
#100 Mortar	2 ½"	12"

The same spiral-wound mortars are often loaded with crackers, display-grade salutes, or consumer-grade color shells. Single comet mortars are not as common in the United States as they once were, due to a combination of regulation and foreign competition. The consumer-product regulations, which have cut down on the amount of composition that can be sold in one mortar tube, do allow multiple small tubes to be sold as a unit. American manufacturers have long produced three-, five-, and nine-shot comet batteries, with all of the tubes glued to a single base, but most of the market share for fireworks of this class has been captured by multi-tube "cake" items (Photo 15-22), mostly made in China. These cakes use cheap parallel-wound mortar tubes, plugged with clay and connected with visco or similar delay fuse. After being connected and loaded, the tubes are tied into neat round or square bundles and labeled. Most cakes have at least sixteen tubes, and some contain more than a hundred. They are made in display sizes for professional use, as well as consumer sizes for sale to the public. Cakes may contain spinners, whistles, ærial salutes, or miniature star shells as well as comets, but the same basic design principle applies to all of them.

Large single comets used in display work usually do not come pre-loaded in mortars. Instead, they are fitted with lifting charges, wrappers and quickmatch leaders like shells (*q.v.*) and are dropped into reusable mortars of steel, heavy cardboard, or polyethylene. Comets are one application where metal mortars are to be preferred, since the large volume of hot gas and dross will hasten the demise of the other types. The vast majority of these comets are made to fit a three-inch mortar, although four-inch are catalogued, and even larger ones are occasionally made. They often end with a heavy report or a shower of colored stars. Comets of this size must be very durable in order to withstand the stresses of firing; they are made on hydraulic presses and are often paste-wrapped for extra strength. Sometimes a perforated felt wad is used to protect the bottom end of a comet, which is more vulnerable than that of a shell. The exposed, burning composition also contributes to the gas pressure in the mortar, and it is important not to use too much lift powder. One ounce of coarse powder (such as FFA) is plenty for a 3" comet weighing one pound or more.

One practice which deserves censure is the predilection of some American manufacturers to label their comets "stickless rockets." Large exhibition rockets have not been regular articles of commerce in the United States for many years. Comets can easily be mistaken for rockets by the uninitiated, but manufacturers were not in the habit of mislabeling them when the selection of actual rockets included large powerful ones. Today the awkward "stickless" term, besides suggesting a safety advantage, is presumably meant to remind display operators that a three-inch comet is the best they can do when they want the thick rising tail effect of a rocket. The fact remains that a comet star is *not* a rocket, but a projectile. It does not continue to accelerate after leaving the firing tube and does not perform like a skyrocket. Furthermore, true rockets can be stabilized without sticks, and in fact were sometimes made this way centuries ago. Confusion and misinformation about fireworks is already widespread enough without the use of deliberately inaccurate terms.

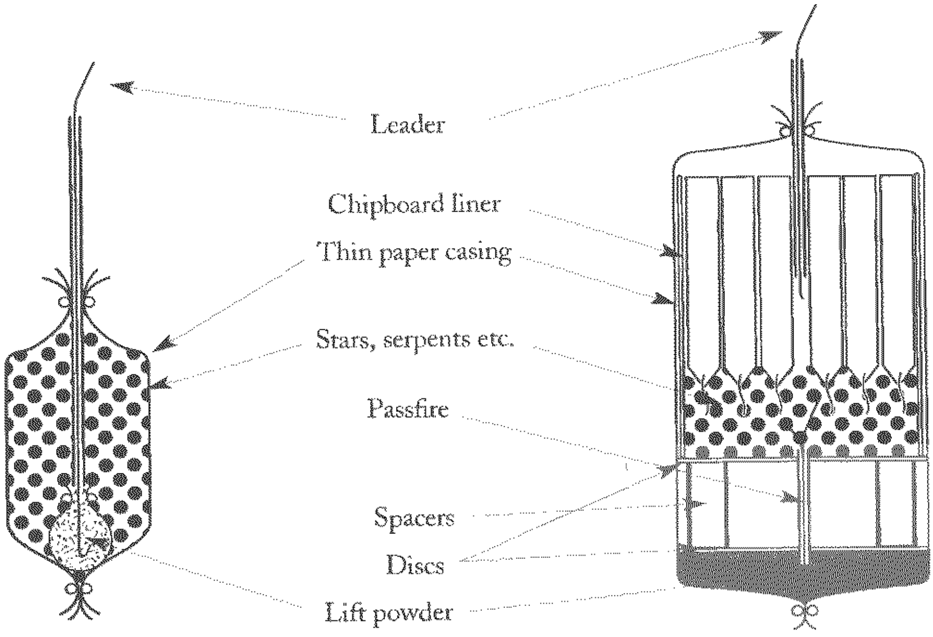


Fig. 15-5. Mines. Left: Traditional mine bag. Right: Meinhart/Bregel type, for large mines

Mines

Mines fire multiple projectiles at a single discharge from a mortar tube. This term probably was derived from military land mines, since both devices produce an explosion at ground level with a spray of rising material. Use of this word in fireworks is mainly a feature of English and does not translate well into other languages. The Italians, for example, call fireworks of this kind *sbruffi*, which literally means sprays of water. Some authors, perhaps wishing to lessen any association with explosives which maim and kill people, prefer the term *starmines*, but stars are not the only projectiles used. One perennial favorite is the use of serpents and similar tube items; the initial burst of flaming objects is enhanced when they begin their "swimming" movements. Various types of crackers and report units are also commonly included in mines. Some consumer fireworks fall into this classification, although the word "mine" itself is rarely seen on a label in an American shop. Commercially-made mine bags are sold for use in professional displays, and are especially likely to be used in exhibitions put on by firework companies themselves. Such mine bags are fitted with quickmatch leaders like shells (*q.v.*) and are loaded into reusable mortars in the same way.

The design of mines is something that tends to be slighted, among hobbyists as well as professional manufacturers. There is a temptation to use "floor sweepings" of practically any kind of inexpensive stars on hand, and other components left over from shell making. When done intelligently, this can be a productive use of materials which would otherwise go to waste. But even though mines do not require the exacting construction of rockets or fancy shells, they are not so simple that quality control can be ignored, and it becomes more important as the size increases. A three-inch charcoal or tremalon mine is likely to be successful with any construction method which keeps the lifting charge under the stars. Many other types of stars can be troublesome in mines and require careful regulation of the lifting powder. Colored stars, especially those made with perchlorates, are easily "blown blind;" that is, they either do not ignite at all, or the muzzle velocity is so great that they are extinguished by the wind. Some energetic, fast-burning stars may create so much pressure when ignited in a confined space that they burst the mortar tubes. The often fearsome reputation of chlorate colors might suggest that these stars are unsuitable for mines, and mines containing ammonium perchlorate stars have caused violent mortar explosions, but the biggest offenders are streamer stars containing high percentages of flake aluminum, which today usually have potassium perchlorate as the oxidizer. When aluminum stars (whether based on chlorate or perchlorate) are used in mines, the stars should not be too small, and extra care should be taken to see that they are hard and tough. At best, such mixtures produce a tremendous amount of heat when ignited in a tube by a charge of black powder, and if inadequate binding allows stars to crumble, the mine becomes little more than a large flash cracker. Even with nitrate stars, serpents and noise units, mines of six-inch and larger calibers cannot be expected to perform well with thoughtless or sloppy construction. One technique favored by successful makers of large mines is the use of a collapsible wad (Fig 15-5, right). Made from chipboard discs with spacers of spiral-wound tubing, such wads provide a pistonlike gas barrier and also help cushion the ærial effects from the shock of the lifting powder.

The term "starmine" is used in Japan to signify something rather different (Photos 15-23 and 15-24), bearing similarities to the western shell finale. This sort of starmine can be of two basic forms. Both employ racked mortars, staked above the ground, with touch-holes at their bases. In the first form, the touch-holes are connected with piped match. An appropriate amount of powder is loaded into each mortar, then one (or possibly more) shells. When shells of different caliber are placed in the same mortar, the smaller ones are placed on top of the one which fits the bore of the mortar more closely. Typically, one shell of the mortar's diameter might be loaded, with extra smaller reports or color shells thrown on top. When the match is ignited, the shells ascend instantaneously for a short, spectacular effect.

In the other form, the idea is to produce a longer display of, perhaps, 30 seconds. Pieces of time fuse are cut to a series of lengths, each differing by a very short duration from its neighbor. These are threaded through the touch-holes of the mortars in order of length and matched together. Time fuse is drossy enough that there is no need to match or prime the end projecting into the mortar, where it nestles in loose powder. The mortars are loaded with powder, shells, and small garnitures as in the first version described. The lengths of time fuse are matched

Table 15-31. Roman Candle Compositions.

	1	2	3
Potassium nitrate	50	53	56
Charcoal, air float	31	17	4
Charcoal, 80-mesh	-	17	4
Charcoal, 20-mesh	-	-	16
Sulfur	16	8	13
Calcium carbonate	-	-	3
Wood meal	-	1	-
Dextrin	3	4	4

NOTES: These compositions are to be dampened with 15-20% of their weight of water, and granulated through 12- to 16-mesh sieves.

together in such a way that all take fire at nearly the same time, but since each is of a differing duration, the shells are discharged in an orderly progression.

Roman Candles

For reasons which are difficult to fathom, the term *Roman candle* is sometimes used in a flippant or mildly derogatory way, to refer to almost any type of firework or projectile firing device. Articles on waterfowling sometimes apply the term to 3" or 3½" magnum shotshells, presumably in an effort to make them sound sensational. The otherwise punctilious *Guinness Book of World Records* once listed an unsuccessful giant-sized *shell* as a "Roman candle." It is not always easy to tell whether this slang usage is intentional humor or is merely a consequence of regulation and urbanization. It does not seem to have been common in the days when fireworks of all types were more freely sold to the public, and Roman candles vied with rockets for the number-one sales position. At this point in time, there may actually be readers who are not quite sure what the Roman candle does. Those who have never fired one or seen one up close could understandably have a mental image of something mysterious and vaguely dangerous. Fortunately, the term is accurately defined in *Webster's* as "a cylindrical firework that discharges at intervals balls or stars of fire."

The name *Roman candle* does not appear in works written in English until the early nineteenth century, but the devices themselves are far older. There is no reason to suppose that they date back to classical Rome, but they were apparently in use in Italy in the Renaissance period. Kentish[128] uses the term "Italian streamers" to specify candles made with tailed stars only, which also suggests that these fireworks are an Italian invention, or at least that the English believed them to be. Early references call them "star pumps" or "fire pumps." Robert Jones, whose work[125] was several times reprinted and much plagiarized, was still using the latter term toward the end of the eighteenth century, when the French were already calling them "chandelles romaines." Whatever the name, the design has been

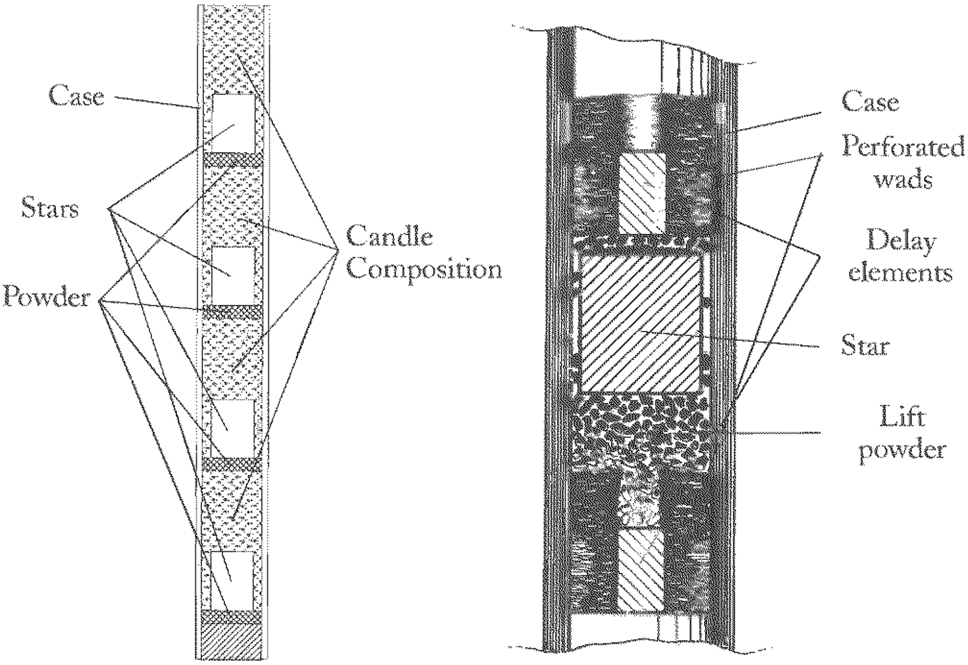


Figure 15-6. Roman candles. Left: conventional Roman candle using candle composition. Right: large-bore Roman candle using felt wads.

popular all over Europe for many centuries. In fact, *firearms* on this principle were made at least as far back as the seventeenth century[258]. Some of these weapons used special perforated bullets which were filled with a delay composition. In their purest form, "Roman candle guns," like the fireworks, kept on firing until all the shots had been discharged, and they must have been a handful for the shooter! Some firearms historians apply the term more loosely, to weapons in which the charges are loaded one on top of another but are fired one at a time, either by separate locks or by one lock which slides on a railing (this type is understandably more common than the all-or-nothing model). It should be noted that "Roman candle gun" is a term adopted by antique collectors living in the nineteenth and early twentieth centuries; it is not what the inventors called these oddities when they were new. Still, it is evident that the collectors chose this name because they thought it would be intelligible to almost anybody; the weapons in question do have the same distinguishing characteristic as a Roman candle, namely, *superimposed loads.*

The classic type of Roman candle (Fig. 15-6, left) is made with a slow-burning saltpeter mixture, called *candle composition* or occasionally *candle fuse* (Table 15-31). As with so many things in fireworks, candle composition varies according to different manufacturers' preferences. That with a high percentage of sulfur is inexpensive and consolidates well, but it has the disadvantage of producing a lot of hot dross that causes the tubes to burn through sooner. Usually a substantial

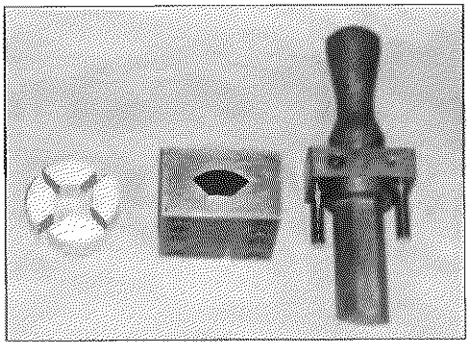


Photo: Michael S. Swisher

Photograph 15-18. Quadrant comets and pump. Comets, at left, fit 4 per ring in a 2" shell insert; sleeve of pump, at center, and plunger, at right, are disassembled to show details.

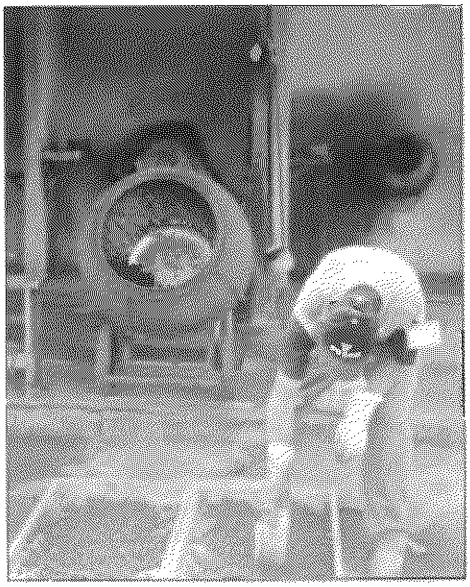


Photo: courtesy Cienfuegos Ltda.

Photograph 15-19. Round star production using a rolling machine.

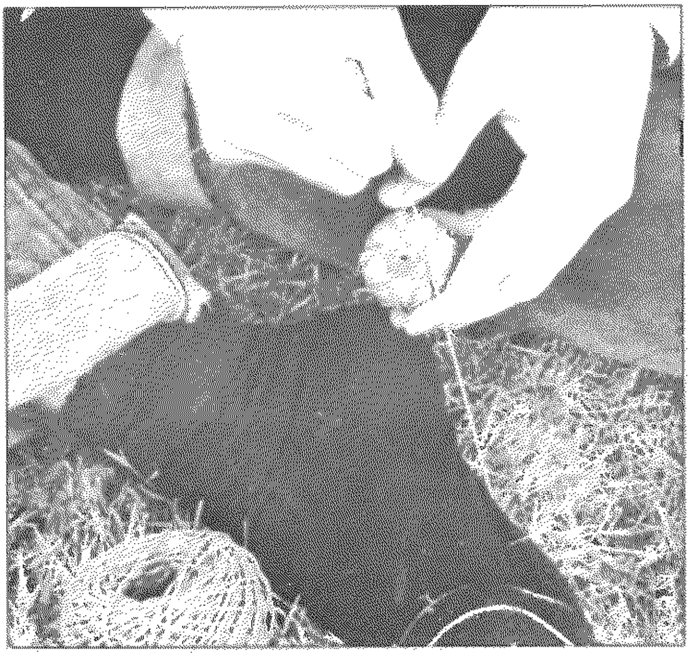


Photo: Jeremy Clayre

Photograph 15-20. Making rai *by the hand-tied method. String is looped around the foot of the worker, who is seated on the ground in traditional Japanese fashion; the hands are left free to hold the report unit and tension the string.*

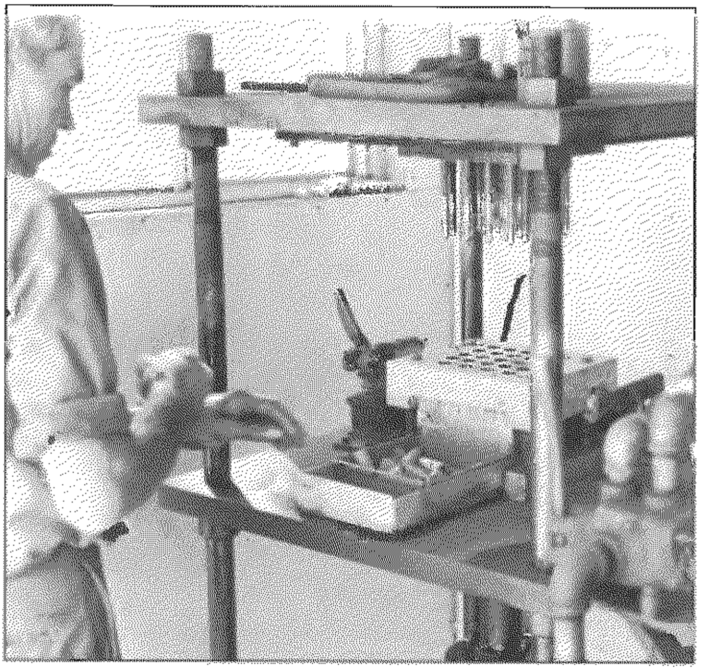


Photo: W.R. Withrow

Photograph 15-21. Gang-loading of garnitures.

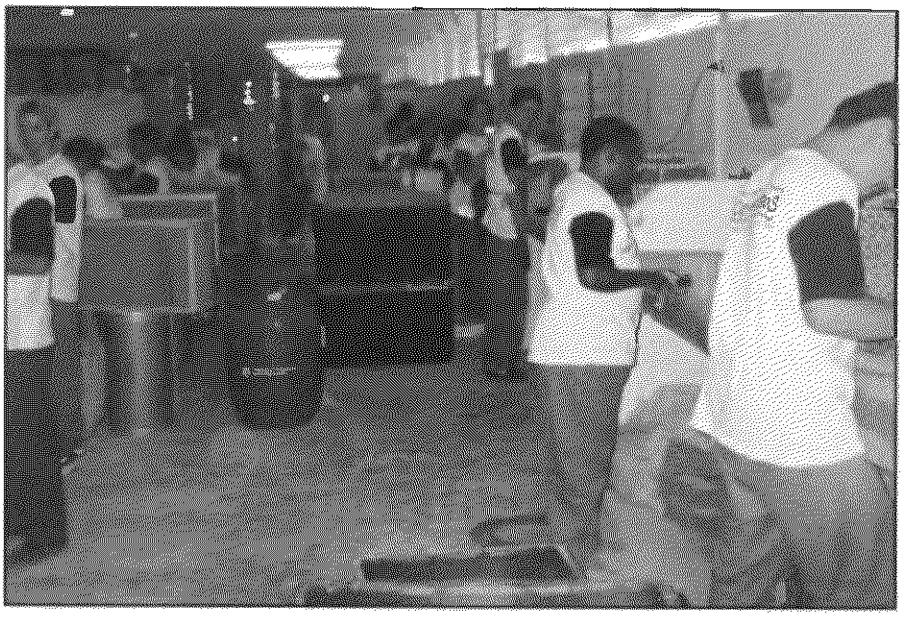


Photo: courtesy Cienfuegos Ltda.

Photograph 15-22. Assembly of multi-tube devices.

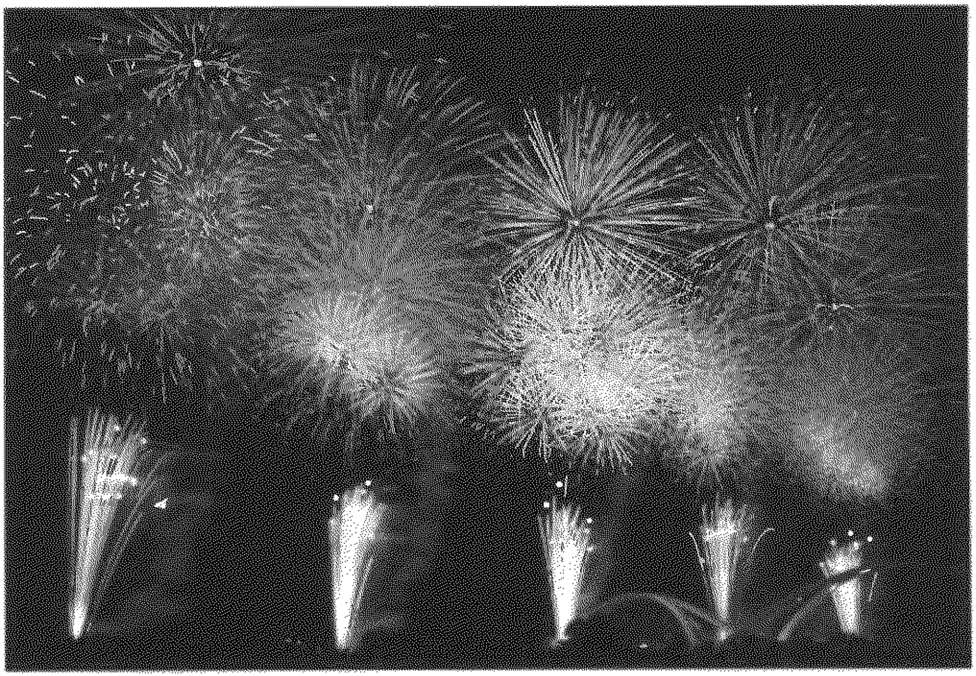


Photo: Kiminari Onozato

Photograph 15-23. Japanese starmine of five colors (Aoki)

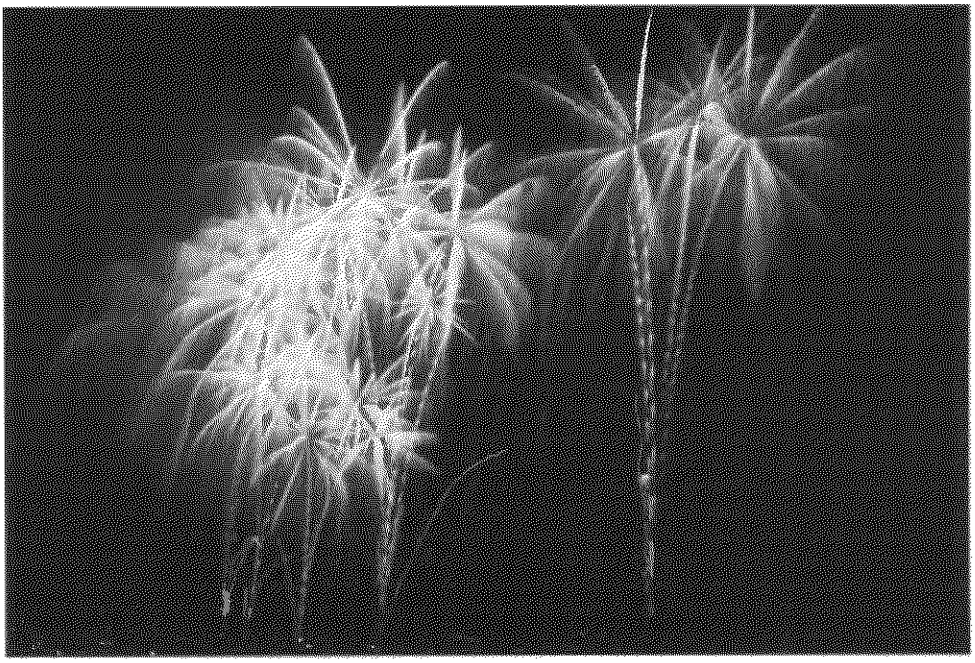


Photo: Kiminari Onozato

Photograph 15-24. Japanese palm tree starmine.

PLATE XII

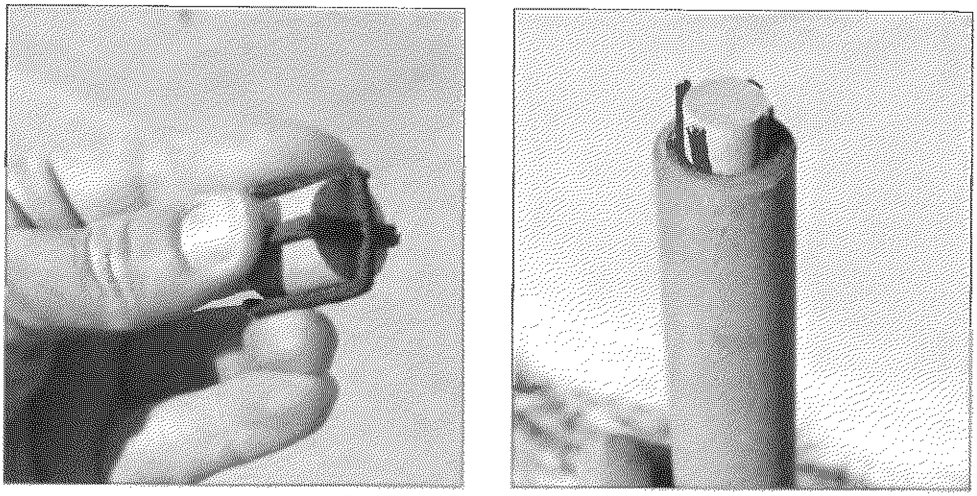


Photo: Barry Bush

Photo: Barry Bush

Photograph 15-25. Match crossed over bottom of candle star and folded at sides (left); star started in Roman candle case (right).

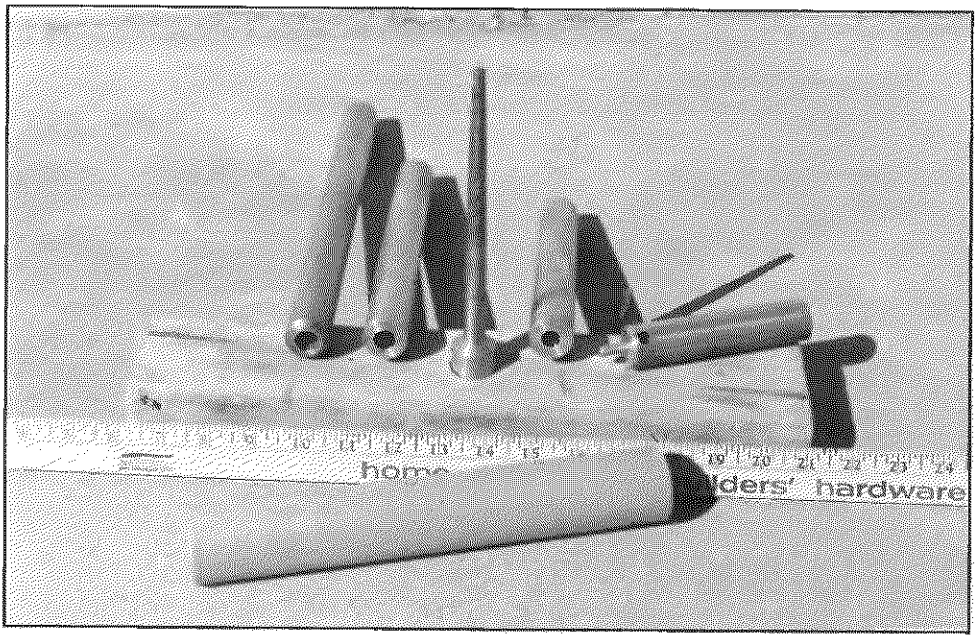


Photo: Barry Bush

Photograph 15-26. Rocket spindle and rammers, including special rammer for forming clay plug with hole at top.

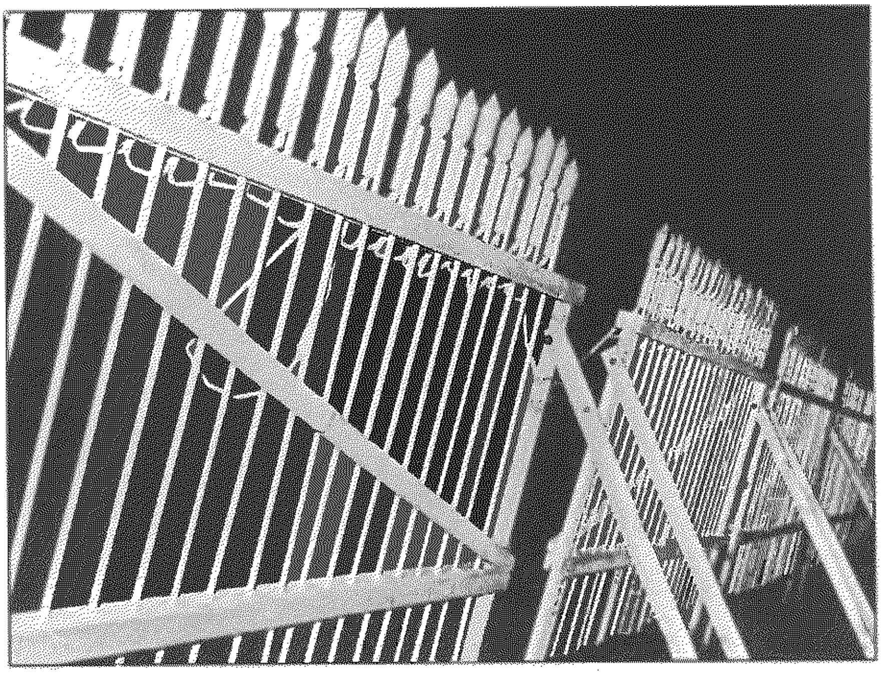


Photo: Ing. Alfred Pokorny, Pyropa Pyrotechnik

Photograph 15-27. Rockets racked and matched to fire as a flight.

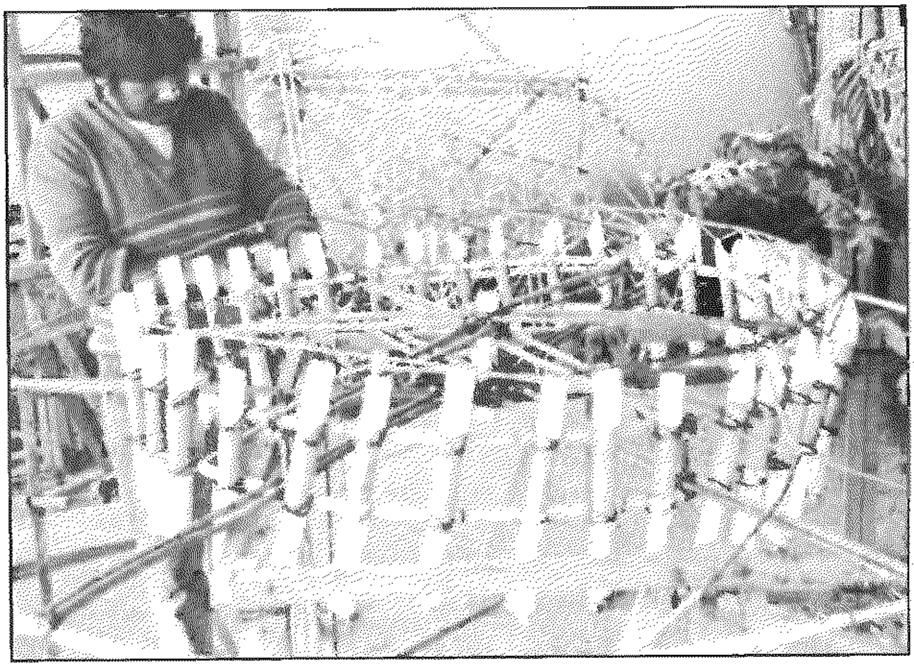


Photo: Alex J. Schuman

Photograph 15-28. A large girandola.

PLATE XIV

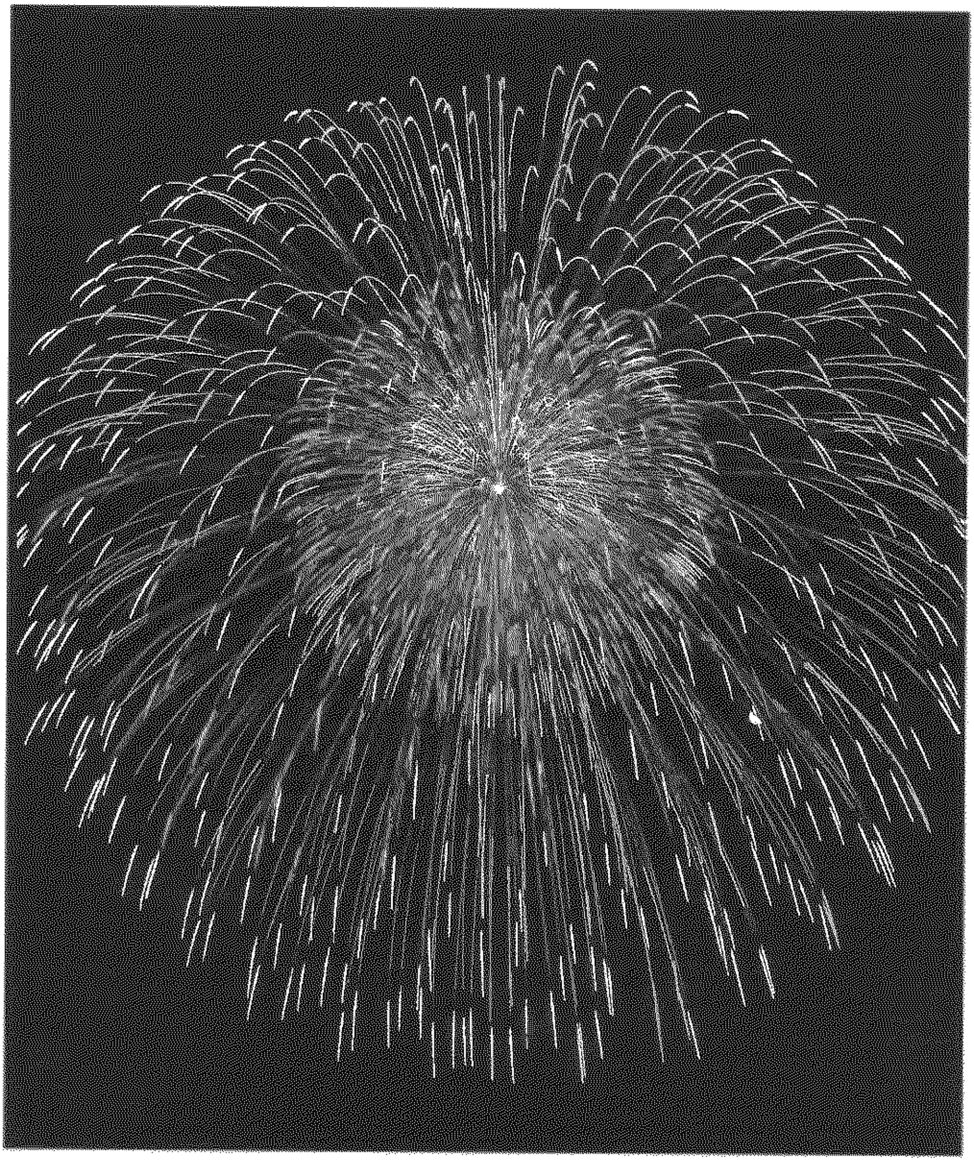


Photo: Kiminari Otozato

Photograph 15-29. 12" peony with color changing pistil (Komatsu)

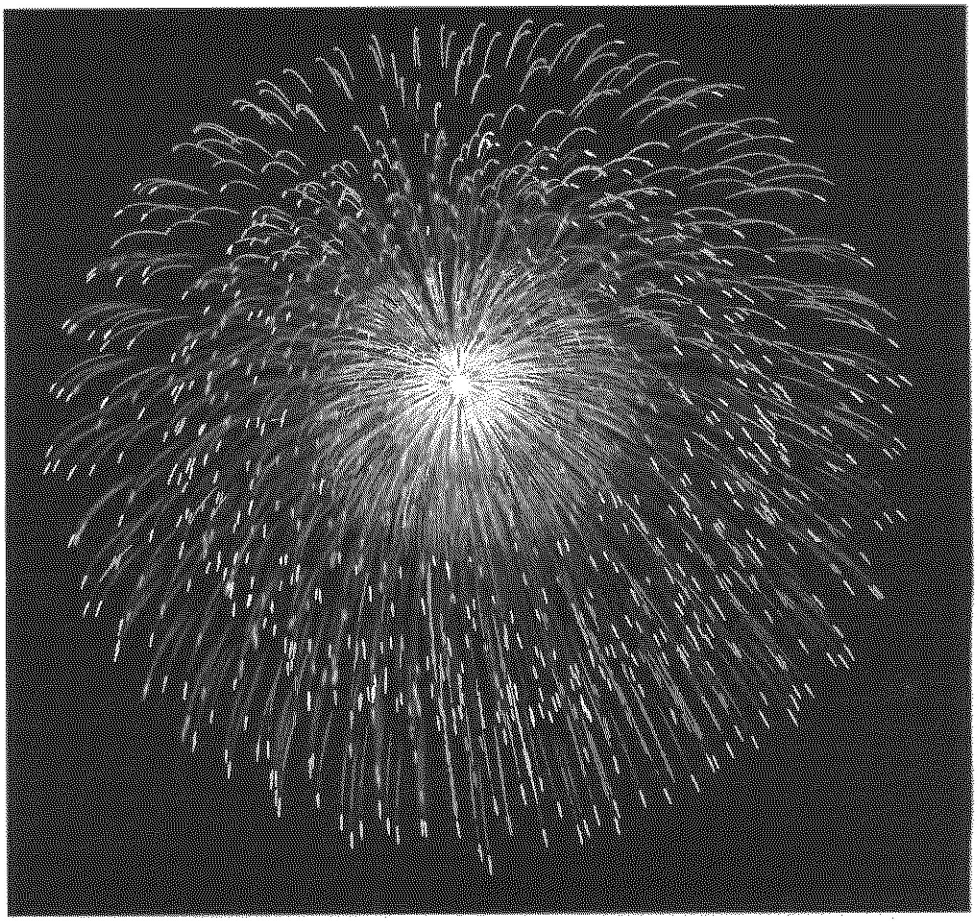


Photo: Kiminari Onozato

Photograph 15-30. 12" double-petalled peony with pistil (Nomura)

PLATE XVI

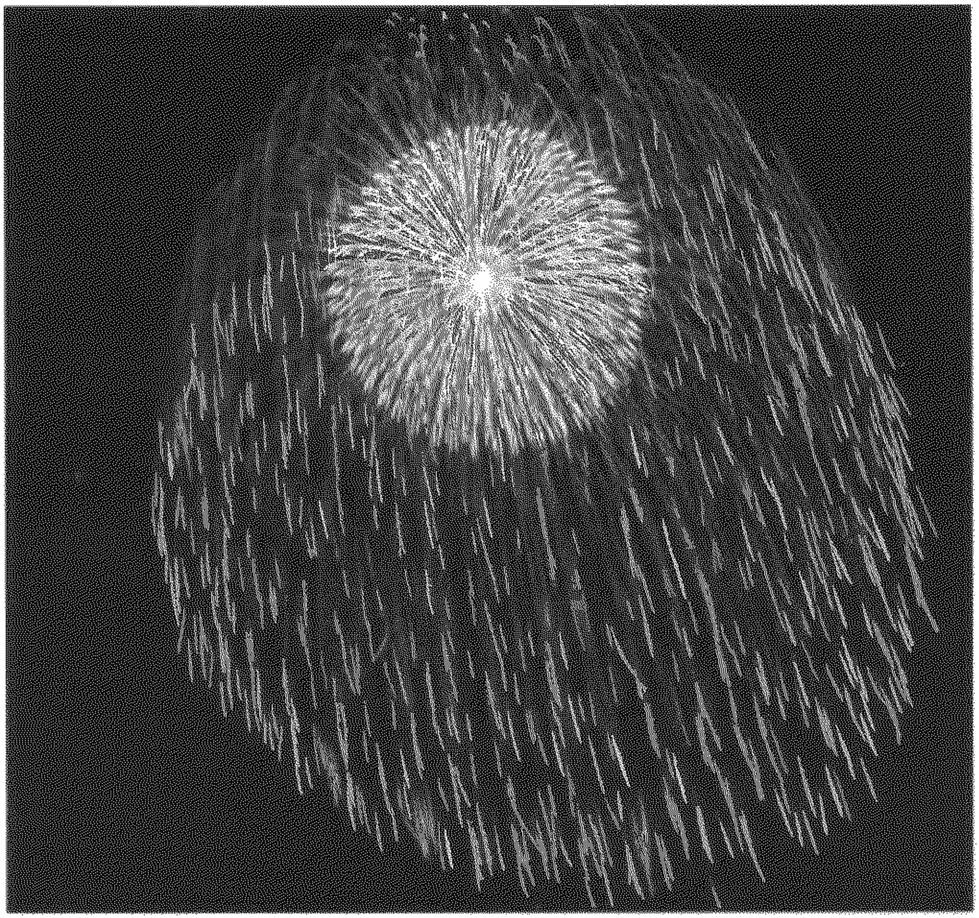


Photo: Kiminari Onozato

Photograph 15-31. 12" brocade willow with pistil part of the charcoal is granular (such as 80 mesh or 36 mesh), which is not as bulky or dusty as the fine powder, and helps produce a good display of sparks in the intervals between stars. Sometimes there is concern about potential problems with friction, when the sulfur-containing powder has to be rammed on top of chlorate stars. Lancaster[139] provides a candle composition that contains no free sulfur, and is intended specifically for this purpose. Most of the traditional mixtures include a small percentage of dextrin, so the composition can be granulated by a wet process, making it easier to handle and measure out into convenient portions.

A Roman candle is charged from the muzzle, requiring the effects to be loaded in reverse order from that in which they are intended to burn. The bottom plug is usually solidly rammed clay, although in some small candles a piece of wooden doweling is glued in place to form both plug and handle. A charge of grain powder must be loaded first, followed by the star or other projectile which slides freely down the tube. Exact dimensions vary, but in general, a suitable pumped star will be 1/16" to 1/8" smaller in diameter than the bore of the candle; the gap may be greater in large exhibition sizes. At this point it is usually desirable to do something to enhance rapid fire transfer. If this is not done, the stars may burn in place for an excessive length of time, causing erratic performance and contributing to the destruction of the paper casing. In small candles, a charge of fast-burning powder, just enough to fill the gap around the side of the star, is the usual remedy. This composition may be called the "inflamant" (if it is given a name at all) and contains a high percentage of gunpowder; straight commercial meal works well. Another method which is very satisfactory with larger candles is to place crossed pieces of bare match under each star when loading it; the match should be cut just long enough to reach the tops of the stars (Photo 15-25). Once a star is properly prepared and seated, it is followed by a charge of candle composition, which is then consolidated. The correct amount of pressure is determined by much experience, and varies according to the size of the candle and the type of composition used. Obviously, the charge cannot be rammed so hard as to damage the star or other projectile, or to crush the inflamant into a solid mass, which would defeat its purpose. Yet each increment of candle composition must be solid enough to serve as a "mortar plug" for the charge of gunpowder and the star that goes on top of it. Appropriate and consistent ramming of the delay composition is one of the most challenging aspects of traditional Roman candle manufacture.

Another peculiarity of these fireworks is that they represent the only type of "gun" in which the "barrel" becomes longer with each shot. A propelling charge barely adequate for the first star in the tube may well be excessive by the time the fourth or fifth one is reached. To accommodate this situation, it is the recommended practice to use progressively larger lift charges as one approaches the muzzle. A few writers in times past have advocated varying the size of the star, to use tighter fitting ones near the muzzle, but this method is not very practical and is rarely if ever used. The cost and complications of having several different star pumps for each size candle are more than most pyrotechnists would care to accept, even if the method offered any real advantages. Furthermore, the change in burning characteristics from one star composition to another can have a greater influence on the appropriate lifting charge than would be seen from a few thousandths of an inch difference in the stars' diameter. It may require a great deal of trial and error to achieve a proper balance between all these factors.

As is true for the internal combustion engine, if Roman candles had not been so well established for so long, they could be regarded as a rather bizarre idea, and there is a seemingly endless list of things that can go wrong with them. England's Rev'd. Ronald Lancaster[140], who is well known for his expertise in this area, describes a good Roman candle as one in which "each of the stars will come out at regular intervals with a sharp little crack, gain a good height and just turn over before it is extinguished." While such perfection is rare in the small candles sold to the public, American-made ones were traditionally quite good. One well-known brand had nicely isochronized stars and fired them consistently to about fifty feet, a good altitude considering the size. The main shortcoming of these candles was that the star colors were limited to red and weak green; this is not a reflection on the maker so much as a consequence of C.P.S.C. regulation, which bans chlorate stars in Class C fireworks. In the early part of the twentieth century, the selection of American-made Roman candles was not so limited. They were amongst the first types of fireworks to be made in large quantities using mechanical assistance, as far back as the 1880s. Combination rammers, like those illustrated by Weingart[249], took as many as 72 casings at a time, and the increased productivity helped place Roman candles among the most popular consumer fireworks. Such machinery is still in use, basically unchanged in form. Weingart lists sizes from one-ball, which hardly seems worth the trouble, to a 30-ball version which was three feet long. His 20-, 25-, and 30-ball sizes had half-inch bores, and, if they performed well, they were a remarkable achievement for commercial practice. Today even candles made for competitions or professional displays, although larger in caliber, rarely have more than twelve or fifteen shots. Roman candles which are carelessly made, or damaged during shipping, can easily burst, although the explosion is usually not too destructive. They carry the warning *Do Not Hold In Hand*, but this is not very well observed, since half the fun with the Class C size is being able to direct the fire. Roman candles have always been high on the hit list of anti-fireworks groups, and in fact are banned in many states. Federal rulings limiting the amount of composition in consumer fireworks have also had a major impact on Roman candles since Weingart's day. Those now available rarely exceed 7/16" bore; five-ball, eight-ball and ten-ball sizes have been the rule for many years. It is interesting to note that the dimensions of these middle sizes are almost exactly the same as those tabulated by Weingart and others, more than fifty years ago.

The practice of listing Roman candles by the number of "balls" they shoot has led to some understandable confusion that is worth dispelling. A colored star of almost any shape produces a flame which is practically round, or in everyday parlance, a "fireball." Many people assume that Roman candle stars are ball-shaped; there are even some "informative" articles in magazines and encylopedias with drawings depicting the stars as spherical! This is not the usual practice, and it never was. Thomas Kentish[128], arguing in 1878 in favor of cylindrical *shells*, reminds his readers that "no one would think of making a Roman candle star like a marble." Through the years, various pyrotechnic authorities have advocated cylindrical candle stars with longitudinal holes to improve ignition and burning qualities. This refinement may have advantages with some star compositions, and one tool maker currently offers pumps to produce such perforated stars. However, the great majority of Roman candles have always been made with plain cylindrical stars. Even in the Orient, where rolled spherical stars are almost universal, the projectiles used in Roman candles are commonly cylinders. One notable exception occurs when color-changing stars are used.

The traditional method using candle composition works very well in Roman candles up to ¾" or 1" bore. With larger sizes it becomes more problematic, so these "exhibition" candles are normally made with a different technique. The charges are separated by means of thick felt wads that contain integral delay elements, usually pellets of composition fitting snugly in their central holes (Figure 15-6, right). In some cases, a specialized delay composition may be compressed into a stout tube at the center of the wad. This may be considered a variant of the spolette or Roman fuse, described under the heading of ærial shells. More commonly, a suitable length of time fuse is inserted through a hole in the center of each wad, the protruding ends being primed or cross-matched. This method is obviously much more time-consuming than the use of candle composition, but it can be cost-effective in these large devices, which may cost ten dollars or more. The wads give more consistent results with large comets and also help protect the projectiles from the lift powder gases. Compared with pressed composition, wads are less likely to be shaken loose during shipping, which would result in bursting or "machine-gunning" when the candles are fired. Exhibition-size Roman candles are not usually made with plain colored stars; often they contain various types of fancy comets such as crossettes or married comets. They may feature almost any type of cylindrical insert, including those which spin, whistle or explode. Almost as popular as comets are small bombshells, complete with delay fuses which allow them to reach peak altitude before they burst into colored stars. This variation of the Roman candle is often called a "bombette" candle.

Many of the small Chinese candles sold to the public employ yet another technique to achieve separation between shots. This involves the use of a tissue paper fuse, like that found in Chinese firecrackers, and in some more recent examples, crudely-made visco fuse, running the entire length of the tube. Increments of granular clay are pressed into place between the stars or other projectiles, and are blown out one by one as the fuse reaches each live charge. In its favor, clay is very inexpensive and does not count as firework composition under the regulations which limit the weight of material in each item. Unfortunately, many of the Roman candles made by this method are quite weak and irregular in performance, shooting their stars only a few feet into the air. Another disadvantage is that the paper fuse can be sheared off during ramming, causing the candle to stop burning with several charges left – a problem which does not occur with the traditional "candle comp." To their credit, the Chinese do produce a lot of good quality candles by this method, which have added variety to the world of consumer fireworks. Some of the best ones do not use plain stars, but are miniature "exhibition" candles with whistling or spinning projectiles.

Rockets and Related Devices

Rockets, despite the many complexities in their manufacture, are amongst the oldest pyrotechnic devices. Their use both in entertainment and in warfare dates back to the Middle Ages, and possibly much further. Although a great variety of rocket motors have been designed, especially within the past 150 years, the kind most common in fireworks differs very little from those illustrated in their oldest surviving descriptions.

The classic rocket composition is a variant of black powder containing excess charcoal, often in particles of 80 mesh or coarser, rather than fine dust. Saltpeter content typically ranges from 60% to 65%. Albertus Magnus, one of the first Europeans to write about black powder, endorsed a 6-2-1 ratio for both rockets and crackers. One Arabian rocket propellant, also from the thirteenth century, contained an unusually high 69.5% saltpeter.[182] A common Chinese recipe was 4-2-1, or about 57% saltpeter, while Congreve's war rockets of the early nineteenth century used 62.4%.[149] These propellants are not milled like black gunpowder, and it is this, as much as the excess fuel content, which gives them a much slower burning rate. The traditional skyrocket is also notable for having a tapered cavity through most of the length of its powder charge, in order to increase the burning surface. Many authors state that the powder column should be perforated for

Table 15-32. Black Powder Rocket Compositions.

	1	2	3
Potassium nitrate	60	60	58
Charcoal, air float	20	22	25
Charcoal, 36-mesh	10	–	–
Sulfur	10	10	12
Extra-fine meal	–	–	5
Aluminum, flake (*e.g.*, U.S. Aluminum #813)	–	8	–

NOTES: In Formula 1, adjustment for speed is accomplished by varying the proportions of saltpeter to charcoal, keeping the sulfur constant, or by varying the two types of charcoal. Less saltpeter and more charcoal will slow the composition; more saltpeter and less charcoal will speed it. Formula 2 is a variant in which part of the charcoal is replaced with aluminum flitters, to give a more brilliant spark effect. In Formula 3, speed is adjusted by raising or lowering the quantity of meal powder; more for faster, less (or none at all) for slower.

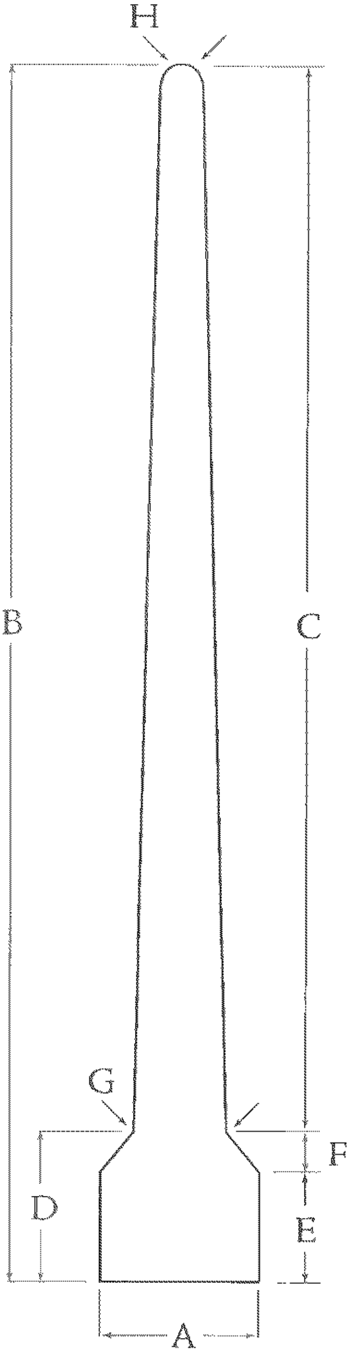
Table 15-33. Rocket Case Dimensions

American Size	I.D.	O.D.	Case Length	British Size
4 oz.	1/2"	3/4"	5" or less	1 oz.
8 oz.	5/8"	15/16"	6 1/4" or more	2 oz.
1 lb.	3/4"	1 1/8"	7 1/2"	4 oz.
2 lb.	7/8"	1 3/8"	about 9"	8 oz.
3 lb.	1"	1 1/2"	10"	8 oz. or 12 oz.
4 lb.	1 1/4"	1 7/8"	12"+	1 lb.
6 lb. or 8 lb.	1 1/2"	2 1/4"	15" or more	2 lb.

about six-sevenths of its length, with the final seventh being solid powder. In former times, this cavity was sometimes called the "soul" of the rocket, a fitting analogy, since there is nothing tangible in it, yet the rocket has no "life" without it. It is often suggested that the core-burning design was adopted because in early times there was little or no truly fast-burning powder, comparable to today's commercial meal. This is plausible, considering that the purification of saltpeter was difficult and laborious, and the modern type of wheel mill was not in use in the middle ages. However, the fact that this ancient design has remained in use for so long is not purely a matter of tradition; it has practical advantages. Powerful rockets can be made from inexpensive hand-mixed powder that does not require time-consuming milling. The surplus charcoal would represent inefficiency to a military engineer wishing to fire a missile as far as possible, but in a firework or signal rocket the long golden tail makes a positive contribution to the display.

As mentioned earlier, the rocket nozzle or choke was traditionally formed by constricting the parallel-wound casing with twine while it was still damp. Apparently, this method is still widely used in some countries, and may have points of superiority. The shape of the pulled-in choke bears a close resemblance to that of more modern rocket nozzles, especially when the relatively low exhaust velocity of hand-mixed black powder is taken into account. Kentish[128] recommends a refinement in which a small amount of clay is rammed in the convergent portion of the choke to protect the paper from the stream of hot gases. For decades, most rockets have been made with rammed clay chokes. In most of these, the shape is theoretically not very efficient, but in practice it serves well enough, and skyrockets of 1" to 1 1/2" i.d. go higher than most other fireworks. Some signal rockets are choked with nothing more than a metal washer crimped in place.

Skyrockets are usually loaded on a spindle having a gradual taper (Fig. 15-7), in order to make them easier to remove when finished. The base of the spindle is normally one-third to one-half the diameter of the inside of the casing. If made with the old-fashioned pulled-in chokes, the cases are, of course, dried thoroughly before being charged. With the more common machine-made tubes, the clay nozzle is formed *in situ*, using the same spindle which makes the core in the powder charge. Skyrockets require a series of special rammers called *drifts* (Fig. 15-8), each of which fits over the spindle rather closely at a given stage of



A = diameter at base of spindle
B = overall spindle length
C = length of tapered portion
D = overall length of base
E = straight portion of base
F = tapered portion of base
G = diameter of spindle at choke
H = diameter of spindle at tip

Figure 15-7. Rocket spindle dimensions

Table 15-34. Rocket Spindle Dimensions.

Rocket Size (inside diameter)	1/2"	5/8"	3/4"	7/8"	1"	1 1/4"
Case Length	5"	6 1/4"	7 1/2"	8 3/4"	10"	12"
A. Diameter at base of spindle	1/2"	5/8"	3/4"	7/8"	1"	1 1/4"
B. Spindle overall length	4"	5"	6"	7"	8"	9 1/4"
C. Length of tapered portion	3 1/2"	4 3/8"	5 1/4"	6 1/8"	7"	8 1/4"
D. Overall length of base	1/2"	5/8"	3/4"	7/8"	1"	1"
E. Straight portion of base	3/8"	15/32"	9/16"	21/32"	3/4"	3/4"
F. Tapered portion of base	1/8"	5/32"	3/16"	7/32"	1/4"	1/4"
G. Diameter at choke	1/4"	5/16"	3/8"	7/16"	1/2"	5/8"
H. Diameter at tip	1/8"	5/32"	3/16"	7/32"	1/4"	5/16"

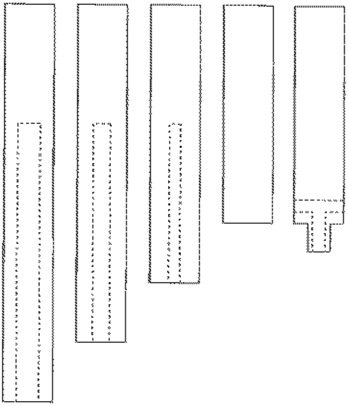


Figure 15-8. Rocket drifts (rammers).

loading. Because the spindle tapers, each successive drift has a smaller diameter hole. Usually there are at least three of these bored-out rammers, in addition to a solid rammer to consolidate the final increments of composition over the top of the spindle. The first drift may be angled at the end in order to give a better shape to the throat of the nozzle; the others are squared off like a normal solid rammer (Photo 15-26). If the same drift were used for the entire loading process, especially on large rockets, by the time the powder level reached the tip of the spindle, there would be a significant gap between the spindle and the solid walls of the rammer. This would mean that the powder nearest the spindle tip was not properly consolidated, and could result in irregular performance or even explosion. At the same time, it is vital that the worker avoid changing drifts too soon, lest one jam on the spindle or damage its tip. As with most other tubular fireworks, the height of each compressed increment of rocket powder should be no more than one diameter. In large, high-performance rockets, the increments may be proportionately smaller because consistent loading density is especially important in these devices. Hand ramming is a knack which requires practice, and even an hydraulic press has to be used with care. Inadequate or uneven compaction will leave the powder soft and crumbly in spots, while overzealous use of the mallet can result in cracks running through an otherwise dense and solid charge. Either of these situations is likely to make the rocket explode when ignited. In rocket motors of this type, the peak thrust is achieved within one or two seconds of ignition. The solid powder column above the spindle contributes very little thrust, and is primarily a delay allowing the rocket to reach its maximum altitude before bursting. Thus the depth of the solid portion depends on the size and purpose of the rocket, as well as the individual batch of composition. In small rockets, up to about ½" bore, the compressed powder may have enough physical strength to act as a "bulkhead" until it burns through. In larger ones, much better timing is achieved when a layer of clay is rammed on top of the powder. This clay can be drilled with an ordinary bit to allow for the transfer of fire to the heading. However, once the final dimensions have been determined, it is usual to employ a special top rammer with a small hollow tip (Fig. 15-8, rightmost; Photo 15-26, rightmost). This tool consolidates the clay and leaves a hole in it, all in one operation. Rockets of ⅜" bore and under may be rammed solid, then finished by piercing to form the cavity. This technique has been in use for centuries; some variation of it is used by the Chinese in their tiny "bottle rockets," which rank among the most popular consumer fireworks in states where they are permitted.

Even the proportions of skyrockets have not changed very much over the centuries, although they do vary a little from maker to maker. Kentish in his *Pyrotechnist's Treasury*[138] explores these proportions in great detail, and gives the standard ratios as follows:

Internal diameter of case	1
External diameter of case	1½
Length of case	8
Length of spindle	6
Bottom of diameter of spindle	⅖

Weingart[249] describes rockets which are longer in proportion to their caliber, with case lengths approximately ten times the bore diameters instead of eight. Whether because American commercial manufacture of rockets dwindled to insignificance not long after Weingart's book was last revised, or because his work has proven so popular among hobbyists, proportions similar to his are still in common use in the United States. A set of ¾" rocket tools, made by a well-known supplier, has a 5½" spindle, a full inch longer than is called for by Kentish's formula, and is meant for a case length of 7½ inches. All of this makes sense when we consider that many of Kentish's compositions contained meal powder, while those used by Weingart (and most of his followers) do not. Faster compositions require shorter spindles, larger vent holes, or both. Another consideration is that even when the spindle proportions are exactly the same, small rockets can use a slightly faster powder than large ones. This is one of the reasons why old works on pyrotechny give so many different compositions for rockets. Weingart went so far as to recommend that part of the saltpeter be granular in rockets of 1½" bore and larger. In practice, one can make good skyrockets in all the normal sizes, from ½" bore up to 1" or 1¼", with the same composition. However, when trying to adjust for maximum performance, the balance can become more delicate.

To illustrate, a series of rockets was made with the mentioned ¾" tooling, keeping all dimensions as much the same as possible. Powder composition was

60% potassium nitrate, 30% charcoal, 10% sulfur in all cases, the only variable being the use of six different kinds of charcoal. Willow, grapevine, and hemp charcoals gave notably more acceleration and greater altitudes than the standard hardwood charcoal powder which is widely used in the fireworks industry. Burning time of the fastest was 1.8 seconds less than the standard, a long time in the life of a skyrocket. Later, some of these powders were used to make 1¼" rockets on an hydraulic press. The tool set available had been adjusted for a composition containing a small percentage of meal powder, and as expected, the rockets containing only standard charcoal gave barely adequate performance. The ones with willow charcoal made an unusually loud roar, and required about 50% more solid powder over the spindle to allow them to reach full altitude. Those made with vine charcoal exploded, and could not be used until their nozzles were relieved with a drill bit. Interestingly, the *linear* burning rate of the vine charcoal composition differed little from that of the willow charcoal version, but the willow charcoal used was a very bulky, flaky material that resulted in a low loading density. The same size casings, pressed at the same pressure setting, held about 20% more by weight of the grapevine powder, and the resultant gas production was more than the casings could stand. Bearing these considerations in mind, it is pointless to list extensive recipes for compositions to be used in different sizes of black powder rockets, as many old firework books do. Nonetheless, the compositions shown in Table 15-32 may be taken as points of departure, and are easily adjusted to fit available materials and tooling with a few trials.

While the dimensions of a skyrocket are rather straightforward once one understands them, the names assigned to the different sizes can be very confusing. Rockets have long been designated in terms of "ounces" and "pounds," but those who bother to check will find that the actual weight of the product for sale is not even close to its nominal size. The terminology originated in the days when rockets (and many other fireworks) were rammed in metal moulds. In those days there was not so much difference between military and civilian pyrotechny; many of the men who made display rockets were also gunners, who tended to think of all projectiles in terms of their *external* diameter. It is probable that the ramming moulds were bored with the same reamers used for cannon barrels; indeed some of them might even have been made from pieces of discarded guns. It was decided that the internal diameter of a rocket ought to be two-thirds of its external diameter, a ratio which still for the most part holds true. A bit of rounding-off was inevitable. A quarter-pound lead ball measures just over an inch, and if this is rounded to an outside diameter of 1⅛" the inside diameter of the quarter-pound rocket case becomes a convenient ¾". A one-pounder cannon had a bore of a little less than two inches, and would correspond to a rocket with a bore of 1¼".

It can be seen that, although this nomenclature would always have been confusing to an outsider, it was not arbitrary. Most of those in a position to become pyrotechnists knew the size of half-pound, one-pound, or two-pound artillery as a matter of course. The key dimension of a rocket was its external diameter, and all its other dimensions were easily calculated from this. The same formulæ could be used to determine the dimensions for rockets which did not correspond to any standard size gun, including some so small that they were designated in drams rather than ounces.* As ramming in moulds was gradually abandoned, it became convenient to think in terms of the *internal* diameters of the rockets, but the sizes remained the same. By 1878 Kentish argued, "[t]he names in use enable the makers to understand each other, but they are not mathematically correct, and are of no utility to an amateur." Especially in Britain, the designations of skyrockets have been preserved to this day, long after the spherical cannonball and the gunmetal mould have become historical artifacts. Unfortunately, the story does not end here.

At some point American sizes diverged from the English and European ones, and the American rockets became much smaller for each nominal "weight." It is difficult to find precise details on this trend, but it appears to have occurred in the early twentieth century and was probably a by-product of aggressive salesmanship, with each producer trying to make his rockets sound a little larger than the others. Weingart complained, "[o]f late, the diameters and lengths of Roman candles and rockets have been changed and reduced so often that no standard of sizes can be given..." Actually, Weingart's own sizes correspond closely to those turned out by other American manufacturers at the same period, suggesting that the shrinking of rockets, relative to their nominal size, had leveled out by the period at which he wrote. Manufacture of display rockets in the United States all but ceased by the 1960s, removing any further temptation to "fudge" on the sizes. Weingart's designations remain typical today, as much as there can be said to be standards for anything that is not a normal article of commerce and is made primarily by hobbyists. Current American regulations limit skyrockets sold to the public to ½" bore and 20 grams of composition, yet some Chinese imports are designated "6-ounce," which according to Weingart, meant ⁹⁄₁₆". The system has become so meaningless that it probably should be abandoned, at least in the United States. Typical case dimensions are shown in Table 15-33, while spindle dimensions are as illustrated in Fig. 15-7, and listed in Table 15-34.

When firework people from different countries talk to each other without knowing about this situation, the potential for confusion is obvious. The old American "four-pound" rockets would be "one-pound" in Britain; the actual weight of such a rocket, complete with guiding stick and heading, is approximately two-and-a-half pounds.

When rockets were the predominant form of aerial fireworks, they were made in great variety, and were sometimes very large. One seventeenth-century English reference offers advice for making rockets up to a thousand pounds. Whether rockets this large were actually fired at that time is uncertain. However, there are well-documented accounts of successful flights with motors considerably larger than any powder rockets on the market today. In 1668, Colonel C.F. von Geissler oversaw the construction of 50- and 120-pound rockets, the German pound being a little larger than the English. These rockets were successful and carried

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* Although the pound varied slightly from one country to another, the standards were close enough to allow workers of different nationalities to understand each other.

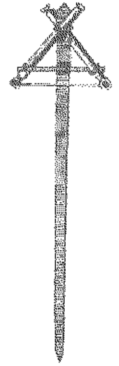


Figure 15-9.
Caduceus rocket (after Jones)[125]

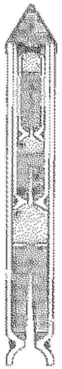


Figure 15-10.
Multi-stage rocket (after Simienowicz)[126a]

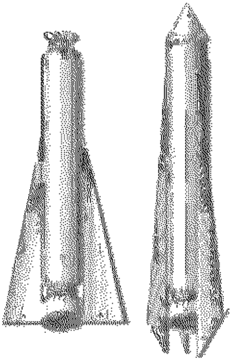


Figure 15-11.
Winged or finned rockets (after Simienowicz)[126a]

16-pound bombs to a considerable distance. Congreve's war rockets, immortalized in the *Star-Spangled Banner*, were not as large as the earlier German ones, but the 32- and 42-pound sizes had a range of nearly two miles.[140] Robert Jones[125] remarks that rockets up to 3½" outside diameter can be rammed well by hand, but larger ones require a machine similar to a pile driver. *The Pyrotechnist's Treasury*[129] mentions rockets up to a nominal 24-pounder, which had a 3¼" bore and would have weighed closer to fifty pounds complete. Even in Kentish's day, however, rockets larger than 1½" to 2" bore were uncommon. The task of carrying large payloads of stars and other pyrotechnic effects was already being taken over by shells.

As the seventeeth- and eighteenth-century illustrations show, many types of fancy or composite rockets were in use. One of the most popular was the caduceus rocket (Fig. 15-9) with two motors attached to a single stick at angles to give upward propulsion, but also rotation around the vertical axis. This produces a double helix of fire which resembles the intertwining serpents of the ancient medical symbol. Multi-stage or "step" rockets have also been in use for centuries (Fig. 15-10). As modern military forces know, this technique allows one to achieve much longer ranges than are possible with single-stage rockets of comparable size and construction. In 1855, Colonel Boxer adopted the two-stage design for a type of lifesaving rocket, which carried lines from the shore to sinking ships. However, the technique was used much earlier to add variety to firework displays. Jones remarks that "they are called Towering Rockets, on account of their mounting so very high."[125]

There are very old references to methods of firing rockets from underwater. The use of fins or vanes to replace the archaic guiding stick is another variation which has been "rediscovered" many times. Davis[64] states that this type of rocket has "recently come on the market" but the same thing was probably said two or three centuries earlier (Fig. 15-11). Fins, or as they were often called, "wings," can be more aerodynamically efficient than a stick and are less sensitive to cross-winds; for military use these are very significant advantages. However, finned rockets take longer to assemble and are difficult to start on a straight path without having a dedicated launching rack for each size. Sticks are simple and inexpensive, and are quickly and easily attached to the rocket casings. The greater weight and drag of the traditional stick is rarely a problem in display work. In fact, a good 1¼" or 1½" skyrocket will go higher than most shells, and sometimes disappoints because its relatively small burst of stars is so far away! In recent times, "Class C" rockets with fins have become quite popular; there is a convention of calling them "missiles," and their resemblance to the military types is undoubtedly a large part of their appeal. Some of the body tubes appear quite large, but they are subject to the same composition limits as the more traditional skyrockets. Often these missiles are equipped with eyelets and are meant to be fired from a brass or steel launching rod, to help overcome their tendency toward erratic flight.

For centuries, rockets were the main kind of ærial firework, and all major displays featured them in large numbers. Unusually large or fancy types were exhibited one at a time, but one of the most popular and spectacular uses of skyrockets was the "flight" or "bouquet." It was common practice to fire dozens, or even hundreds at once from specially constructed racks or flight boxes. (Photo 15-27) One particularly grand display in London in 1749 had 100,000 one-pound rockets in the finale alone! A Paris display of 1893 featured a bouquet of 15,000 rockets of unspecified size, and flights of a mere thousand were not too uncommon before World War II. Most people still think of rockets when they see ærial fireworks; some can be shown the shells and told what they are, and will still call them "rockets." However, shells had already begun to dominate the ærial scene during the Victorian era. Today, especially in the United States, skyrockets are hardly seen in professional displays. A single-break three- or four-inch shell can carry as much material as the old American "four-pound" rocket, and for most effects, the altitude attained by the latter is not worthwhile. Large rockets are more troublesome to ship than shells: aside from the potential for damage to the propelling charge, the sticks make them awkward to handle. The main factor in the demise of rockets has been concern over falling sticks and casings. While the danger posed by sticks has been exaggerated, there is the *potential* for serious or even fatal injury when the stick of a large rocket remains attached to its body. At best, the sticks and casings cause more litter than is evident with good shells, but this does not seem to cause too much concern in other lands. Great Britain is known for its very strict laws on firearms and explosives, but skyrockets are still common in British firework displays. Rockets are even more popular in Spain, Portugal, Mexico, and many South American nations. Quite large ones of ¾" to

1" bore, usually tipped with salutes, are used by the general public and may even be launched from the hand! Besides a strong cultural preference for rockets, most of these countries have a completely different attitude towards insurance and litigation than we find in the United States at the present time.

While the core-burning skyrocket is still the preferred type worldwide, many other designs have been used in pyrotechny. End-burning black powder rockets are made with commercial meal powder, often with a little excess charcoal or other material to regulate the burning rate and give a good display. This type is usually pressed by machine and is popular in Germany and some other European countries. According to Ronald Lancaster[139], "[t]hese rockets do not look as attractive as traditional rockets since the gold tail is reduced, neither do they go as high, but they are easier and cheaper to make." End-burning motors are more tolerant of slight variations in the composition, and if well made, they have good physical strength. These characteristics make them especially useful for signal rockets.

Whistling rockets have become popular among the firework-buying public. A whistle tube may be attached to the outside of any size rocket for a combination effect. However, the term "whistle rocket" generally refers to a device in which both sound and thrust are generated by the same mixture. These rockets usually have a small cavity at the rear of the propellant charge, but it is not as deep as the cavity in a traditional rocket of the same size. Whistle compositions produce more energy than any type of black powder, although the fact that whistles lack the choke or nozzle keeps the actual specific impulse well below the theoretical yield. Commercial whistling rockets are small, only ¼" to ⅜" diameter, and are usually made with plastic tubes. Whistling rocket motors can be much larger than this; hobbyists often make them with a 1" to 1¼" bore, using standard rocket casings which have been cut shorter. Some of these rockets are quite powerful and produce a deep, mournful howl worthy of a wolf, or the legendary banshee. Unfortunately, even when made by experienced workers, they are sensitive to handling, changes in ignition methods, and other factors, and they can be very destructive should they explode. Because of the danger level, it seems unlikely that they will become commercial products.

Pyrotechnic artists who are not manufacturing for commercial sales may use a variety of exotic propellants, ranging from castable mixtures to the zinc and sulfur powder popularized by model rocket clubs. Adding iron or steel filings to a standard black powder rocket is an old variation, which gradually fell by the wayside because the hard particles tend to damage ramming tools and may cause enough friction to be hazardous. Nonetheless, metal powders have made a comeback, and today, titanium is the most popular of these additives.

One unusual firework which is currently popular among hobbyists is the strobe rocket. The propellants employed are derived from compositions for strobe stars, and generally contain ammonium perchlorate, magnalium alloy, and other ingredients. The flashes can be almost any color, and in addition to the unique visual effects, these motors produce a sputtering or chugging noise much like that of a single-cylinder engine. They are loaded on a shortened spindle, as are the large

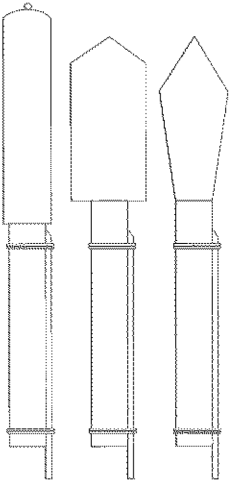


Figure 15-12. Various forms of rocket headings. Left: "faux-fourreau;" center, cylindrical pot of larger diameter; right, divergent cone.

whistling rockets, but the strobe type normally has a clay nozzle. Strobe rockets carry limited payloads due to their intermittent thrust, and they are almost as prone to accidental explosion as the big whistlers. If they are kept small, the danger is minimal and it is possible that they could become consumer products. At present, strobe rockets must be considered a novelty, but it was not long ago that the same could be said of whistling rockets.

For special exhibitions, rockets may have elaborate headings, such as multiple breaks, timed reports and other effects described more fully under shells. However, even in the nineteenth century, a simple load of stars and powder was the rule. The thin casing that holds these terminal effects is often called the "pot," and may or may not be fitted with the familiar conical cap. Many commercial rockets contain only a few stars, which can be held in the cap alone. Somewhat more can be accommodated in a few turns of paper rolled onto the rocket and tied off after filling, the so-called "faux-fourreau." When a full payload is used, the top end of the rocket casing can be built up with a strip of chipboard so it will mate to a burst casing of larger diameter. A similar approach uses a divergent cone, so that the rocket head is largest where the cap is attached (Fig. 15-12). Large skyrockets, which may ascend to a thousand feet or more, are particularly attractive with long-burning streamer stars. Another simple heading which is always popular is the flash report. Such rockets can be dangerous if they malfunction, but the risk is mostly to those firing them. Although it is a coincidence rather than a matter of design, they even have a safety advantage. The explosion of a large salute will often shred the rocket casing, and at the very least, the kickback will break the stick or detach it from the casing. This destroys the aerodynamic stability of the spent rocket, so that instead of falling at high velocity, it becomes relatively harmless bits of litter.

Since rockets can carry cameras or live animals without damaging them, it is not surprising that this method of propulsion is traditionally chosen for the more delicate firework components. At one time, it was not unusual for the head of a large rocket to contain several small ones. Use of soft-cased "silent" flash inserts or *relampagos* has already been mentioned. However, one of the truly classic rocket effects is the parachute flare. Parachutes can certainly be used with success in bombshells, but the relatively thick, strong casing which is necessary in order for a shell to withstand its lifting charge adds to the difficulties. The pots of rockets can be made with lightly constructed tops so that the contents pop out the ends with very little force, just what is needed in the case of parachutes. Even with this advantage, parachutes require careful construction and loading. Silk, cotton and synthetic fabrics can all be used, but most parachutes in commercial fireworks are made of tissue paper. Handmade tissue is to be preferred because it has no "grain" and is not therefore likely to take a set when it has been folded for a long period of time. The pyrotechnic material is suspended on stout twine, usually cotton, of sufficient length to keep the parachute safe from sparks. Usually the effects consist of one or more flares, although they may be cascade cases, smoke units, or small spinning devices. Whatever it may be, it is placed in the rocket head atop a mild blowing charge, usually a small amount of coarse grain powder or even a rolled-up piece of bare match. The live material is then covered with sawdust, bran, or other filler. Packing a parachute is a skill which requires practice; the usual procedure is to fold it into a narrow wedge and then to roll it lightly into a cylinder, finishing by wrapping the shroud lines around the paper. More bran or sawdust fills the empty spaces in the rocket head. Rockets with parachute flares are still used occasionally for signalling, and when rockets are seen at all in modern American displays, they are often the parachute type. A further refinement which can be very attractive is the use of a long chain of small lights instead of one large one. In addition to the usual complexities of parachutes, a chain has to be rolled up in such a manner that it will unroll completely after being ejected, without burning through the cord. Since the regular spacing of the lights is very evident in the air, much of the effect is lost if one of the flares falls off or fails to ignite. The technique is quite difficult to master, but the use of rockets instead of shells helps make it a little more reliable. Good examples of these fireworks are available from Spain.

The term *girandola* or *girande* was sometimes used in the past to mean a volley of separate rockets, more commonly called a "flight" or "bouquet." However, to most pyrotechnists, the girandola is a rocket-propelled wheel. In light of modern-day mythology, it is amusing to note that these rather obscure and capricious fireworks were also traditionally known as "flying saucers." The frames are usually made from rattan or bamboo strips, which are flexible enough to be formed into wheels and are strong in relation to their weight. The central boss of the wheel has a smooth, round hole which slides over a spike or guide rod on top of the launching pole. A small girandola may only have rockets attached to its rim, at about a 60-degree angle, which spin as well as lift the wheel. Larger ones use driver cases in the same manner as a fixed wheel, and have rockets, sometimes dozens of them, affixed at right angles to the rim, the central boss, or to intermediate points of attachment. They may be equipped with colored fire pots or lances as well. Usually, the fancy girandolas are designed to turn for a considerable length of time on the ground, like an ordinary horizontal wheel, before the rockets ignite. Some of them even have specially made rockets, or relays of rockets, which cause them to hover in the air, or descend and then re-ascend. Finally, the structure may carry a bombshell, or more commonly, each rocket has a heading which bursts at peak altitude. If anything goes wrong with the balance or timing of a girandola, the flight can become highly erratic, and the size and weight of these pieces demand alertness from the spectators. Clearly, no pyrotechnist should even consider tackling girandolas until he is able to made good wheels and consistent, powerful rockets. In any case, it is pointless to give exact specifications, since — outside of commercial manufacture, where prefabricated plastic wheels, complete with holes to accept the rocket motors, are often economical and reproducible — each one is a custom project. In the United States, girandolas are made only by a handful of hobbyists. They are more common in countries which have many artisan pyrotechnists and a strong tradition of rocket-making, Mexico being the most noteworthy example (Photo 15-28). One American enthusiast, Tom Dimock[49], notes that "in Mexico, injuries suffered during fireworks shows are considered a badge of honor. In the United States they are considered cause for a major lawsuit."

Tourbillion is the classical name for a modified rocket which rotates in a horizontal plane; the term is taken from the French word for whirlwind. Another early term for these fireworks is "table rockets," since they are best fired from a hard flat surface. More recently, the small ones sold to the public have been given a great variety of names. Since the Second World War, two of the most popular American brands have been the "Buzz Bomb" and the "Helicopter," and these have become practically generic names for tourbillions as far as the consumer is concerned. Most of these devices are about ½-inch i.d. and four inches long; the Chinese ones are made in great variety and include some as small as ¼" × 2". The "wings," made of plastic or chipboard on Class C tourbillions, seem to inspire a lot of misconceptions. Twisted or beveled edges suggest that the wing acts as an airscrew and is responsible for lifting the device. Inexperienced users are often observed to stand tourbillions on end when firing them, and are then perplexed when only about half of them fly. These fireworks should always be laid flat on a smooth surface, as it is the vertical vector of the exhaust which causes them to fly. Tourbillions were working centuries before gasoline-powered helicopters came on the market, and most of the old ones used simple flat sticks.

Table 15-35. Tourbillion Compositions.[39]

	1	2	3	4
Homemade meal powder	50	50	-	40
FFFFg sporting powder	35	36	-	40
Meal D	-	-	80	-
Iron filings or ferro-titanium, 20-50 mesh	10	-	-	-
Charcoal, air float	5	7	20	-
Aluminum, flitters (U.S. Aluminum #813)	-	7	-	-
Aluminum, atomized (Reynolds #120)	-	-	-	10
Sodium oxalate	-	-	-	10

NOTES: The home-made meal powder is a mixture of 75 potassium nitrate, 15 charcoal, 10 sulfur, ball-milled dry for 12 hours. FFFFg sporting powder is equivalent to FFFFFFFA fireworks powder, but glazed. Iron filings require treatment to prevent corrosion if the device is to be stored for more than a few days.

Some makers preferred short pieces of wooden hoop, because the upward curvature made the tips less likely to snag on uneven ground. This is not to say that angled edges are a bad idea, but the crude ones found in most commercial examples contribute little if anything to their ascent. The "wing" is more accurately described as a counterpoise to keep the tourbillion horizontal, and to prevent the device from flipping over on the ground at the critical moment when it first begins to rotate. Some old references describe tourbillions which had no wings at all; these were clayed and drilled in the centers like saxons and were fired from metal rods.

Tourbillions were formerly made much larger than today's commercial offerings, a typical size being one-inch bore and 8" to 10" long, and these large ones used multiple vent holes (Fig. 15-13). Typically two opposing jets near the end plugs were ignited simultaneously by quickmatch to spin the device. Only when it was rotating at a good rate of speed did the fusing reach the two, sometimes four, lifting jets underneath. Such tourbillions rise almost perfectly vertically and are more reliable than the small single-hole variety, but they require more time and skill to make. Tourbillions traditionally contained iron or steel filings to enhance their effect. They use their propellant (Table 15-35) rather inefficiently, partially on account of the heavy case, as well as on account of the enlargement of the vents that occurs as the gases and flames shoot through them, and cannot fly as high or carry as much weight as skyrockets of comparable size.[79]

Balloons have sometimes been used in connection with fireworks displays to carry such things as cascade cases, wheels, and various designs made from lances. While never a routine part of every small-town Fourth, there was a time when they were relatively common at large exhibitions for world's fairs and other special events. At Chicago in 1893, a balloon carried a lancework American flag

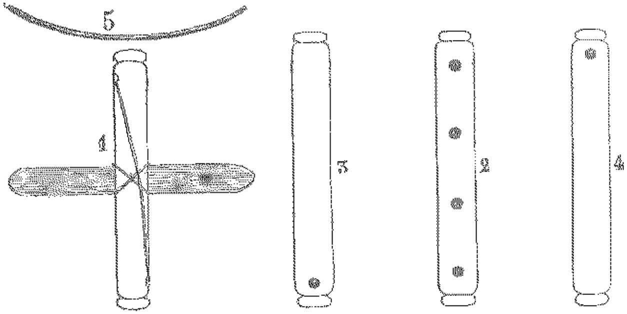


Figure 15-13. Tourbillions. 1 shows assembled tourbillion; 2, lift holes at bottom of case; 3 and 4, spinning holes; 5, stick used as counterpoise.

sixty yards wide and a hundred yards long. A Currier and Ives print of the dedication display for the Brooklyn Bridge in 1883 also depicts a balloon with pyrotechnic garnishment. Even some turn-of-the-century children's literature gives instructions for attaching small fireworks to balloons, which must have made for a few anxious moments among parents and neighbors. At least one U.F.O. hoax of the 1950s used the simple expedient of commercial safety flares, carried aloft by surplus weather balloons. Whether because of fire danger or simple lack of interest, such devices have been very little used in display work in recent times. The revival of dirigibles for use at sports events and other large outdoor entertainments appears to have potential for the pyrotechnist, since these vehicles are so much more controllable than free balloons. It is also worth mentioning that the term balloon or *ballon* was often used in old works on pyrotechny to mean a spherical bombshell, rather than a lighter-than-air flying machine.

Shells

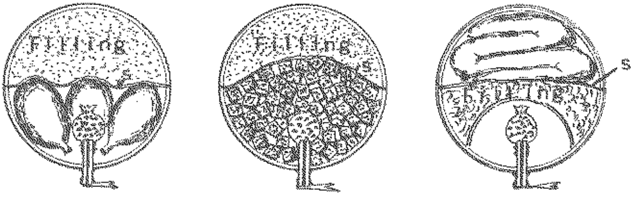
Aerial bombshells are the most popular of all display fireworks; many public displays consist of nothing else. The simple term "bomb" or its cognate is correct in most European languages, but many people seem to find it impolitic and today the word "shell" is more commonly used. Occasionally shells have been made oval – a prolate spheroid is the more precise term – or in shapes resembling a medicine capsule. One accomplished hobbyist even builds square shells, which of course have to be fired from square mortars. They make unusual burst patterns, although he has yet to perfect a square break. In practice, almost all shells are either spheres or cylinders.

Essential to every shell is a tough casing which is sealed against lift powder gases, and a time fuse to delay the shell's burst until it has reached a suitable altitude. The traditional fuse is the *spolette* or Roman fuse, made by ramming powder in very strong parallel-wound tubes. Spolette tubes are normally about ¼" to ⅜" inside diameter and 1½" to 4" long. In some parts of Europe, plastic fuses are common, made as an integral part of plastic shell casings, but this variant is rarely if ever made in the United States. Spolettes are usually filled with straight commercial meal powder, which is rammed hard in small increments for maximum strength and consistency. It is usual to ram the last increment with a pointed tool, or, if using a flat-ended tool, to scratch a groove or drill a hole in the compacted powder. While black powder normally provides excellent fire transfer, such measures are intended to give a longer flame spit in an application where reliability is at a premium. The empty space in the spolette is filled with short pieces of bare match long enough to extend beyond the end of the tube, and a paper nosing is tied to hold the match in place. It is usual to punch a small hole in the paper, between the tube and the ligature, to serve as a gas vent. The matched end of the finished fuse usually projects into the shell's bursting charge, while the flat, bare end of the powder column is on the outside. Properly made fuses of this type are quite sturdy, but for safety's sake, they are placed at the tops of the shells where they will not be subjected to the pressure from the lifting charges. Methods of attaching lifting powder and ignition devices will be discussed later.

When made correctly, spolette fuses are extremely reliable and give very precise timing. These characteristics are particularly important for the secondary effects of complicated multi-break shells containing timed reports and similar devices. However, because of the skill and the time required to make them, spolettes are no longer common as the main time fuses in commercial shells. Cord fuse is ubiquitous in Oriental shells, and the ¼" Chinese and Japanese products are extensively used in other countries as well. Many American makers prefer the ⅜" domestic fuse, which is physically stronger as well as having a heavier powder core. Whichever style is chosen, the ends must be prepared to insure good fire transfer, and there are two basic ways of accomplishing this. The fuse may simply be cut cleanly, preferably at an angle to expose as much powder surface as possible, and then primed with slurry and grain powder. If a water-soluble binder is used, special care must be taken to allow the fuses plenty of drying time, as the fabric layers are prone to retain moisture. The second method, and probably the better one, is "cross-matching," in which a thin piece of bare match passes through the core of the time fuse at approximately a right angle. If this technique is chosen, the correct timing interval is marked on a piece of fuse, which is cut to allow ¼" to ½" extra on each end. When punching holes in time fuse, it is important to see that they are well centered and that a minimum of asphalt is smeared into the powder core. Holes should be made just large enough to accommodate the match, and the fuses should be squeezed after the match is inserted to help hold it in place. This technique requires more time and skill than slurry priming, and can be especially awkward with the smaller Oriental fuses. A common variation is to split the time fuse down to the timing mark, place the match in the cleft, and tie the fuse tightly back together at the end. Many pyrotechnists consider cross-matching more trustworthy than slurry priming, and it has the added advantage that the surplus length at the ends often makes the fuses easier to manipulate, such as when tying on burst bags.

Round (ball) shells are apparently the oldest type, although the ones used in past centuries differ in several ways from the style popular in Japan and China today. Paper is the most common and most versatile material for the casings. In the past, some ball shells, especially large ones, were reinforced by the addition of fabric; this technique is not apparently in use now, but it appears to have merit. Small wooden shell hemispheres were once made for sale to the fireworks trade, as were thin casings of zinc or other metals. Today, moulded plastic hemisphere sets (usually PVC or polystyrene) are available at reasonable cost and are quite popular in sizes up to six- or eight-inch. These sets are easily assembled by painting the joints with a chlorinated solvent such as methylene chloride or trichloroethane, which dissolves enough of the plastic to form its own "glue." Makers with an eye for quality often finish plastic shells with a few layers of pasted paper to promote a more even break and to seal any pinholes around the seam or the fuse area. Plastic hemispheres are primarily a commercial expedient designed to save time; although some attractive effects are possible with them, they are in the minority among exhibition-grade shells. Another disadvantage of plastic is that it leaves shards of litter which are often sharp enough to inflict cuts on members of the public who may pass through the fall-out area later. The manufacture of paper hemispheres has been described elsewhere[139,236], and will be omitted here because most shell makers purchase them from outside sources. They are available in all the standard sizes from 3" to 12", and even ones of 18" or 24" are far from being uncommon. Wall thickness varies with caliber, but the usual style requires a considerable amount of additional paper to make a good chrysanthemum-style shell. In some cases "nesting" hemispheres are used, which consist of an inner set plus an outer set with a total wall thickness about twice that of the plain hemisphere sets. This is one time-saving product which gives good results if managed properly; the paired casings require only two or three layers of thin pasted paper to seal and finish them. Nesting sets are usually available only in the most popular sizes, such as four-, five-, and six-inch hemispheres.

Simple ball shells with rammed time fuses were traditional in northern European countries; such authors as Weingart[449] and Brock[36] emphasized the style as late as the 1940s. Undoubtedly, some pyrotechnists had favorite designs which they did not share with others. As a rule, however, the bursting powder was simply mixed with the garnitures; in the case of a plain star shell, the hemispheres might actually be assembled first and filled through the fuse hole, the time fuse being added last. Additional pastewrapping was minimal; most of these shells were not intended to produce especially hard or symmetrical bursts, and their casings only needed to be strong enough to withstand the lifting stresses. This is not meant to denigrate the old efforts, which, except for the fusing method, did not differ greatly from many shells fired today. With many of the basic effects, such as plain star breaks, salutes, cannonades, or hummers, it can be difficult even for an expert to tell whether the burst was that of a ball shell or a cylinder. However, there are some effects which are peculiar to ball shells, and have been carried to very high levels of artistic refinement. The most elaborate round shells have been perfected in Japan, and are imitated commercially with varying degrees of success in other countries, notably Taiwan and mainland China.



(A) Five reports (B) Willow (C) Comic figure

Figure 15-14. Poka *shells (after Shimizu).*[236]

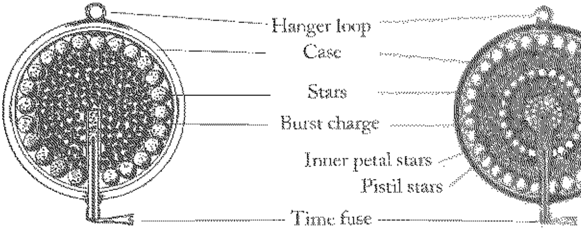


Figure 15-15. Warimono *shells (after Shimizu*[346]*).*
Left: single-petalled. Right: double-petalled.

Detailed information on Japanese fireworks can be found in the works of Takeo Shimizu, which began to appear in English in the 1970s. The most comprehensive and practically oriented is *Fireworks: The Art, Science and Technique*[346] (1981, revised in 1996). Shimizu's writings have been extensively quoted and paraphrased, both with and without attribution, and to such an extent that much recent material published under the general theme of "fireworks" is really only valid when applied to Oriental practice. There have been other meaningful contributions to the literature on this subject by various researchers and hobbyists, some of whom have made "pilgrimages" to Japan. However, considering the great popularity of Japanese-style shells, a few general remarks here should not be amiss.

There is a kind of Japanese shell called the *poka* (Fig. 15-14) which contains only a small bag of bursting powder tied to the time fuse, and produces a softer break than the old European ball shells. Typical garnitures in poka shells include parachutes and inflatable paper figures, timed reports, and an effect called "falling leaves," in which pieces of stiff paper are coated with a slow-burning color composition. However, the epitome of the Japanese style, the *warimono* (Fig. 15-15), uses a powerful central bursting charge to produce a large globular pattern of stars. Symmetry is considered the primary artistic goal, although it may be enhanced by many other features, especially color changes. More often than not, the stars have tails and the shell is called a *chrysanthemum;* aside from the elegance of this effect, the chrysanthemum flower has special significance as the ancient imperial symbol of Japan. The term is often loosely applied to all hard-breaking round shells, but the Japanese are more particular. When stars with no tails are used, *i.e.*, ordinary color stars, the shell is called a "peony" (*botan*). However, two other effects – *kira-kira* (Table 15-25, Formula 1) and the "brocade" or *nishiki* star with aluminum (Table 15-25, Formula 4) – are referred to as peonies as well. Sometimes the brilliant aluminum star is also called a peony – *shiroi botan* – even though it has a light streamer effect. Magnesium stars are usually cut, then coated in the tumbler with a suitable ignition mixture, and are mostly used in *poka* shells. However, if they are carefully made, the round stars so produced are also suitable for the symmetrically-bursting type. Either way, the finished shell is called a "dahlia," a description rarely heard in the United States. The floral terminology is extended to the internal features as well (Photos 15-29, 15-30, and 15-31). Each spherical layer of stars is deemed a "petal," so that a shell may be single-, double-, or in rare cases triple-petalled. A smaller inner layer of stars, or stars mixed more randomly with the central bursting charge, form a "pistil," while miniature shells used as inserts are simply "small flowers." *Palm tree* shells (*yasu*) are made as a chrysanthemum shell, but using large cut stars for the effect. The stars are usually cut in the form of "tablets" from either a fuel-rich pine charcoal/ferro-titanium mixture (for the usual effect) or from a red star composition into which about 15% ferro-titanium has been incorporated, giving the effect of a colored head with a spark tail. Other star shells in the Japanese tradition use the rolled spherical stars described earlier; selection of the proper sizes and burning rates is especially important for these shells.

In general, fast-burning compositions are preferred for peony and chrysanthemum effects; Japanese color mixtures usually contain significant percentages of charcoal, and in some cases they still employ chlorate/sulfur combinations. There is also a Japanese pine root pitch which reportedly[46] gives higher burning rates than most of the resinous fuels available in the West. Even with these reactive materials, the stars tend to be smaller than one might expect. A five-inch shell typically has outer petal stars about half an inch in diameter, while even in a twelve-inch peony, they may not exceed one inch. This design serves two purposes. The Japanese deem it important, in many shells, that the taut symmetry of the "flower" be preserved until extinguished, rather than allowed to droop. To fulfill this condition, the burning time of a shell of normal size cannot be much over two seconds.* Another reason for using small stars is that it improves the fullness of the burst patterns. Warimono shells produce "flowers" approximately a hundred feet in diameter for each inch of shell diameter. In most cases it looks better if the shell break is dense and moderately large, rather than being extra-large but sparse or irregular. An exception to this is the dahlia shell, in which the brightness of the stars is important and visually compensates for their sparsity. Compositions are adjusted so that the stars can be made commercially in a practical manner; however, beginners and occasional makers have a tendency to roll the stars too large. Willow shells may use slightly larger stars, but star count is still important and their effect is mainly due to the use of compositions with very slow burning rates.

The bursting charges used in chrysanthemum-style shells encompass so many subtle variations that their manufacture is practically a specialty unto itself. The commercial granulated black powder so common in other fireworks is used to a very limited extent in Japanese practice, mainly in lifting charges, primings on shells and components, and sometimes as burst in small inserts. The majority of bursting compositions are not used as homogeneous granules; instead they are coated on various inert materials. Rice hulls, cotton chaff, and cork chips of various sizes are the most common, the inert core size being matched to the shell diameter and its construction. For example, a 6" blue peony might practically be made using coated cork chips, while for a 6" blue peony with yellow pistil, the fiercer coated rice hulls may be the better choice. Also, chaff has a purpose even without a powder coating – to fill an inert space, as in the construction of a "Saturn Ring" or "UFO" shell. Coated rice hulls typically carry four or five times their weight of black powder; with the coarser materials the ratio of powder is not quite so high. Shimizu mentions coating burst powder on small stars at the center of a shell (pistil stars), but apparently this technique is not widely used. The use of inert carrier materials in bursting charges lessens the weight of shells, and probably reduces the danger if a shell explodes in the mortar. However, its main function is to make more efficient use of the powder. In large shells especially, powder coarse enough to preclude destruction of the stars would be too coarse to be consumed before the shell casings rupture. At best, much of the powder would be wasted if it were the ordinary type. In smaller shells, black powder of any type is not energetic enough to provide the hard break desired, while using solid grains of chlorate or perchlorate composition would probably be too energetic.

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*It is necessary for willow stars to droop significantly, and peonies are sometimes allowed to droop slightly at the ends before a final flash or silver core ignites.

Both commercial and "homemade" meal powders are used; with the latter, as in skyrockets, variations in charcoal can have a substantial effect on performance. In Japan, the standard is hemp charcoal, which burns rapidly and produces high volumes of gas; economic as well as legal considerations make this material uncommon in western countries. Willow and vine charcoals have comparable reactivity, but the standard "airfloat" charcoal of the American fireworks trade does not, so domestic makers of ball shells usually employ commercial meal powder or resort to non-traditional techniques. In any case, the use of straight black powder for chrysanthemum and peony bursts is at its best in eight-inch and larger shells, and single-petalled sixes. Smaller shells benefit from more powerful powders, the goal in each size being to maximize burst radius without making the result appear sparse or ragged. Chlorate bursting powder is successful in 3" and 4" shells, although a well chosen perchlorate composition serves just as well. A common chlorate burst is referred to by Shimizu[246] as "H-3." Japanese compositions are traditionally based on ten parts of the oxidizer; in streamer stars, for example, "Chrysanthemum 8" contains more charcoal and is slower burning than "Chrysanthemum 6." Thus H-3 indicates 3 parts of (hemp) charcoal to 10 of potassium chlorate, plus the requisite binder to adhere the mixture to rice hulls.[139] Substitution of other charcoals does not seem to diminish the potency of this composition as much as it does in black powder. Some American hobbyists use activated charcoal like that administered as an antidote to poisons; the increased porosity of this product allows it to absorb more oxidizer while the preparation is wet. Bursting charges are commonly made with potassium perchlorate as well. Their burning rates vary greatly depending on the fuels and catalysts used; some are actually slower than black powder, but they compensate by producing a higher volume of gas. Extensive work has been done on such perchlorate mixtures in Japan, because they are considered safer than the chlorate versions, and because they are especially well suited to the most popular sizes of shells, from four- to six-inch.

Japanese Shell Burst Compositions[216]

	H3	KP
Potassium chlorate	73.5	-
Potassium perchlorate	-	68.5
Hemp (or paulownia) charcoal	24.5	17.5
Sulfur	-	12
Soluble glutinous rice starch	2	2

Shell caliber alone is not enough to determine the optimum bursting charge, especially in the more elaborate designs. Fast, hot-burning stars may make a significant contribution to the burst gases, requiring adjustment of the bursting powder or reduction of the final wall thickness to keep all these factors in balance. Multiple-petalled shells generally require more powerful or finer grained bursting powders than their single-petalled counterparts, especially if the latter do not have pistil stars. The main consideration here is that there is simply less room for powder in a multi-petalled shell. It is also common practice to have finer and/or faster powder at the center of such a shell, graduating to coarser material in the outermost layer. For large fancy shells, the bursting charge, *e.g.* black powder on cork chips, may be sieved for uniformity as stars are. The best narrow "cut" of particle sizes can then be chosen for each specific shell design.

Assembly of small single-petalled shells is rather simple, although it must be done carefully to insure that the components stay in position. Usually the bursting charge is separated from the main stars by tissue paper. The stars are arranged in each hemisphere and the bursting charge is pressed in lightly by hand, leaving the halves slightly overfilled. The hemispheres may be clapped together, or a piece of thin cardboard or sheet metal may be placed on the upper hemisphere and held there while it is carefully inverted to meet the lower one. Afterward, the barrier material is carefully withdrawn. If this step is not performed correctly, or if the shell is underfilled, stars may shift inward, and such irregularities will be evident in the burst pattern. When a warimono shell is well filled, there will be a slight gap between hemispheres at first; after applying pressure and tapping with a stick, the contents will compress enough to allow the halves to meet. In the case of very large shells, the worker may actually stand on the assembly while tapping it, making several turns until the settling is complete. Regardless of size, the casing should now feel solid and the contents should not rattle. Rather than joining two identical halves, shells of about eight inches and up are often easier to assemble if a section is cut out of the top hemisphere, that is, the one which does not have a fuse. If this is done, the burst bag is made large enough to hold the entire charge. After filling the lower hemisphere as usual, the partial upper one is attached and the remaining stars are inserted through the hole. The process requires dexterity to make the stars form a single layer against the shell wall, but it makes it easier to insure that there is no empty space at the extreme "top" of the shell. After everything is carefully consolidated, the last handful of stars is layered on top of the burst bag and the "lid" of the casing is glued or taped in place.

Assembly of multiple-petalled shells can become very complicated, but there are essentially two methods which parallel those used in single-petalled shells. When assembling each half, one may use a simple former to press a hemispherical cavity into the bursting charge, which is lined with nothing more than thin paper. Stars and powder are arranged in this space, and if necessary, the process is repeated with an even smaller inner petal. In other words, the shell is built as a set of concentric hemispheres, which are eventually assembled to form concentric spheres. Obviously, if the layers are not well centered and carefully mated, the burst pattern will have a misshapen center which spoils the effect. The other approach to building a multi-petalled shell is to complete the inner petal(s) before assembling the main shell casing. Shimizu[216] illustrates an inner assembly wound with twine to compress and strengthen it. Others use ordinary cardboard hemispheres glued together, sometimes perforated with holes to facilitate even fire transfer to the outermost layer of bursting charge. Such inner assemblies are practically complete shells and could be paste-wrapped and fired from mortars of the appropriate sizes, except that the fuses are simply tubes filled with match or powder for quick fire transfer. The tube has to be attached to the actual time fuse in the outer hemisphere, before the outer stars and bursting powder are added. Care must be taken to center the inner assembly before proceeding. The size ratio of inner to outer petals varies, but is usually around 1:2 or 2:3. For example, an eight-inch double-petalled shell is likely to have a four- or five-inch inner layer. The sizes of the stars in each layer are not necessarily in the same proportion; inner petal stars may be almost as large as main stars, but they do not spread nearly as far. The relative size of the petals in the shell burst is an important aesthetic consideration, as are the timings of any color changes in the petals. This makes the design of large fancy chrysanthemum shells very complex, but when all the factors are properly balanced, the results can be spectacular. Seemingly endless variety is possible, although some combinations of color are naturally more pleasing than others, and their relative brightnesses must also be taken into account. For example, an inner petal of resin-fueled blue stars would be overpowered by an outer petal of green magnesium stars. The reverse, using the brilliant green in the center, makes a very attractive shell if the quality of the colors is good.

After shells are assembled, they require paste-wrapping, which is done with paper strips. The ideal amount varies, but in general, larger shells require thicker casings. Often multiple-petalled shells benefit from more pastewrap than single-petalled ones of the same size, because of the differing capacity for bursting powder. Strips are laid on in such a way as to minimize overlap, and the direction of the paper grain is changed each time a new layer is begun. Various patterns can be used depending on the worker's preference and on whether the grain runs the short way or the long way in the strips. As a general rule, two or three complete layers of 30- to 40-pound paper will be required for each inch of shell diameter, so that a ten-inch chrysanthemum is likely to have 20 or 30 layers on top of the original strawboard hemispheres. Fewer layers of thicker paper may be used to save time, sometimes with a sacrifice in the regularity of the shell walls. Exceptionally large exhibition shells may require over a hundred layers of pasted paper, a factor adding greatly to the time and cost of making them. When all but a few layers of paper have been added, it is usual to wind string around the base of the time fuse to strengthen the joint. On the other side of the shell, opposite the fuse, a loop of heavy twine or small rope is added. The final layers of pastewrap strengthen the attachment of this "hanger," which serves as an aid to carrying and for loading into the mortar in domestic Japanese practice (where lift and leader are rarely attached); and through which the leader is neatly and prosaically passed when shipping away to foreign markets.

The globular shell burst is subject to numerous variations, most of which are straightforward in conception if not always easy to execute. The two hemispheres may consist of stars of two different colors to produce a halved burst pattern; this shell only works well if the different stars are chosen so that they give a similar flame size, and are approximately equal in mass.* These criteria having been met, the shell is open to the usual refinements, such as to have an inner petal, although this tends to make the whole item appear fussy.

Another popular effect in round shells is simply a ring of stars; double and triple intersecting rings are sometimes made. These shells may be described as peony types in which most of the outer stars are missing. The same applies to more exotic pattern or character shells which can form letters, geometric figures such as heart or star shapes, or even animal shapes. Such designs are "drawn" in stars on one hemisphere of the shell, and may or may not be surrounded by dummy stars of non-combustible material. Ring and character shells carry a high proportion of "dead" weight in relation to the number of stars deployed, and they can be appreciated only when they burst in the proper orientation. If the design is seen on edge, it appears to be nothing more than a jagged line of stars. Except for the simple ring, most of these patterns are not very effective in shells smaller than five-inch, while sizes larger than eight-inch are prohibitively expensive and are rarely made. An exception occurs with "Saturn" shells, which combine a full inner "petal" with an encircling ring. Good Saturn shells are very attractive from any angle, are sometimes available in sizes up to ten- or twelve-inch, and may have multiple color changes and other refinements for customers willing to pay the price. Another design which minimizes the disadvantages of pattern shells is the hourglass with ring, which appears to be an American invention.

Shell-of-shells is the name given to a shell containing multiple smaller ones, which produce their miniature starbursts after they have been dispersed by the initial breaking charge. The main shell's burst may be "dark," or other effects such as streamer stars may precede the small insert shells' performance. For obvious reasons, a shell-of-shells needs to be relatively large; in ball shells, the effect is hardly worthwhile in sizes under six-inch and is usually better in larger ones. In shells over twelve-inch caliber, probably the majority sold are of this type. This situtation seems to foster confusion among people outside the fireworks field, such as journalists, who sometimes interpret the name "shell-of-shells" as being some kind of superlative or promotional term, comparable to *crème de la crème* or "the war to end all wars." In fact, it is simply a technical description. It is also worth noting that a shell containing only small reports is not usually called a shell-of-shells, even though the size and appearance of the inserts may be identical to the same maker's color inserts. When inserts are large, more than two or two and a half inches in diameter, they may be made the same as if they were to

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* If not, the two halves differ by more than just the color, since the heavier stars travel faster and further, while the color with the smaller flame envelope appears as "points" rather than as lush color stars.

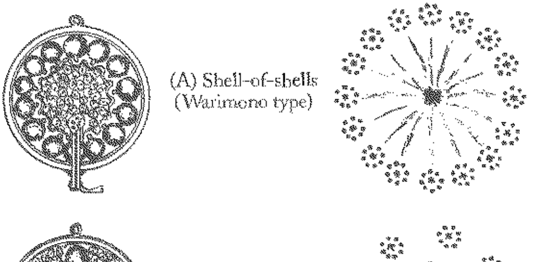


Figure 15–16. Various spherical shell-of-shells types (after Shimizu).[236]

be fired singly from mortars, with stars on the outsides and powder in the cores. As an extreme example, a 36" shell may contain six- or eight-inch double-petalled chrysanthemums. Inserts for ball shells of normal size are of simple design, having stars mixed with the burst powder, and the standard ¼" fuse for timing. They are spheroids from one to two inches in diameter.

In a warimono style shell, insert shells may be used as though they were large stars, comprising the outer layer, the inner layer, or – in 24" shells, for example – both. Alternatively, a few little shells may be buried in the burst charge. A popular design is *koarin* – a willow with small flowers opening in the center after the willow has achieved a large break. In the latter case, they are normally timed to burst after the outer stars have reached their full spread and produced the usual "flower." The miniature shells, normally of contrasting color, have a surprise effect. This style is sometimes described in English-language price lists as "small flowers in relief." Irregular "fusillading" timings can be very effective in these shells. When insert shells fill the outer layer of the large shell, they are usually timed to explode simultaneously, making a globular "bouquet" of small flowers. Most shells of this style are broken "dark," which helps build anticipation, and more pragmatically is a concession to the limited space for bursting charge. Very large examples may have an inner petal of stars. Fig. 15-16 shows the different configurations used.

Report units (*rai* or *banurai*) may be used in the same ways as small colored shells. Japanese practice also includes timed reports, usually in *poka* shells. The obvious variations are possible, but there is a set style used in daylight displays and for signalling, just as western pyrotechnists sometimes use a single maroon to begin and/or end a display. Typically, a single break of such a *poka* contains an odd number of salutes, from three to seven. The details are up to individual preference, but often the final report is larger, and timed to fire a little after the sequence that has been set up by the previous ones.

Parachutes are used more extensively in eastern than in western fireworks, sometimes in unusual ways. Shimizu[26] describes a shell called "willow in the moon," which produces a willow of smoke stars that cannot be seen until a delayed flare ignites. Another effect rarely seen in the United States is *zanko* or "remaining light," which requires the delicate packing of one or more parachute flares in such a manner that they can survive the burst of a warimono shell. After the shell's pattern has developed, the paper wrappings must unravel so that the parachutes can unroll. This can effectively be done for shells of 6" and up, although a skilled maker can achieve it in a 5" shell. The author has seen a 24-inch shell-of-shells in which each of the *poka*-style inserts, perhaps 4-inch in size, contained its own parachute flare in addition to other stars.

Various devices (*kyokudo*) can be attached to the outside of a shell for preliminary effects. The most common are rising tails, essentially pumped comets. They are paste-wrapped like crossettes or transformation comets, but instead of being folded over the ends, the overhanging paper is cut or torn into strips which facilitates firm attachment to the shell casings. The outside ends of such comets may be fitted with dangling pieces of bare match, but they usually ignite well if simply primed. The comets attached to shells in this manner are usually pumped, this being the only frequent Japanese use of such stars. Rising whistles and strobe devices are also in use. A large shell may carry several smaller ones, securely attached to its hanging loop, and timed to perform at brief intervals before the main burst. An uncommon variation is the use of timed flash salutes, woven into a kind of long pigtail that trails behind the rising shell. These are difficult to make and must be loaded and fired with great care. If the device becomes tangled, one of the flash bombs may fire in proximity to the shell casing, destroying the whole assembly.

The Japanese often fire two shells, generally a matched pair, from the same mortar at the same time. They may burst simultaneously but more commonly are timed about two seconds apart. Such pairs, joined by paper wrapping, are occasionally found in the United States, where their appearance has given them the nickname "peanut shells." These are not quite analogous to multibreak cylinder shells, because the ball shells separate as they leave the mortars, and each ball shell has its own time fuse which takes fire from the lifting powder.

The Japanese tradition includes a whole genre of daylight fireworks which is rarely seen in western nations. One type features parachutes and inflatable paper figures; the other involves designs which are analogous to those found in night shells, but are executed in smoke rather than colored fire. There are smoke willows, smoke chrysanthemums and other effects in a variety of colors. Magnesium stars are visible in daylight, especially with their own smoke background, while reports and other noisemakers are effective at any time.

In Japan, 12" shells have been very highly developed and are *de rigueur* in many firework competitions. Six- and eight-inch warimono designs rival the twelves in popularity, but relatively few shells over 12" are made. When they are, the Japanese appear to have little interest in the 16" size and tend to go all the way to 24", a projectile which normally weighs over a hundred pounds. For certain occasions 36" and even larger shells are made, but they are extremely time-consuming in proportion to the effects produced. A few American hobbyists have made such gigantic ball shells, and 24" shells are imported into the United States. Experimentation with these fireworks is prohibitively expensive, and there is more speculation than accurate information about them. In addition, many American display insurance policies require adherence to separation distances established in N.F.P.A. Standard 1123, which effectively rule out the use of shells larger than 12" at most urban display sites. It is not too difficult to find imported 16" ball shells, but many of them are of poor quality and are not as impressive as good 12" shells of domestic manufacture.

Increasing manufacture of ball shells in other countries has resulted in many modifications of the Japanese techniques. The quality of Chinese shells is extremely variable. Those from Taiwan are usually good and the designs conform more closely to those of the Japanese product; one of the best known Japanese makers, Mantsuna, now makes those of its shells which are to be exported to the West at a factory in Taiwan. Experimenters in other countries have developed many hybrids of western and Japanese techniques. Cut stars work well in shells of the chrysanthemum and peony type where a color change is not desired. With some mixtures, such as the old zinc streamers, they are easier to make and ignite better than the traditional rolled stars. The use of flash powders in star shell bursting charges has become common, not only among hobbyists but among Chinese, American, and Spanish manufacturers. Both perchlorate and nitrate mixtures are popular, and one successful maker uses a mixture of black copper oxide and atomized aluminum, which is practically a fast-burning thermite. As a rule, the flash mixture is added in small percentages to a black powder bursting charge to boost the power output. In large multiple-petalled shells, it is used in the central burst bag only. There is some argument over the safety of this technique, and the bright flash is a disadvantage, but it is inexpensive and convenient. Flash burst has become practically universal in Chinese Class C shells where chlorate mixtures cannot be used. Whistle composition is used in a similar way by many American hobbyists. Plastic ball casings are common and a few manufacturers produce high-quality shells from them, including the hourglass with ring and other pattern effects. Gummed paper tape is sometimes used to finish shell casings, but the resultant layers are not as strong as pasted paper, and adjustments must be made accordingly.

Cylinder shells are rarely made in Asian countries, but for a long time they were the most common variety in the United States, and are still the rule in parts of Europe. They are sometimes called "canister" or "can" shells, which clearly distinguishes them from ball shells, but is only strictly accurate for certain types. Cylindrical casings cannot be expected to produce globular bursts, but good symmetry is possible with skillful assembly. A cylinder obviously holds more material than a sphere of the same diameter; this can be considered a disadvantage only in a few instances, as when display operators wish to maximize shell count for commercial reasons. Cylindrical inserts such as comets, whistles, serpents and tourbillions fit much more neatly into cylindrical shell casings than into spherical ones. Also, cylinders may be joined end-to-end to make shells which display multiple bursts from a single mortar shot.

Plastic canisters have been highly developed in Europe but are not very common in the United States. In the past, stout cardboard tubes with wooden end plugs were common, and even "tin" cans were sometimes used. Today, many commercial manufacturers make star shells in spiral-wound casings with wall thicknesses of one-eighth inch or less. The ends may be closed with chipboard discs alone, or with the addition of paper end caps. In the latter case, the filled shells resemble the paper cans in which such household goods as cornmeal are sold. At this point, it is usual to reinforce the assemblies by wrapping with twine, in a manner to be described later. In shells of moderate size, it is possible to omit this step; one very famous Italo-American manufacturer long emphasized his stringless shells with claims that they produced less burning fallout. Other experienced makers disagree, or at least believe that any such concerns are overbalanced by the advantages of strung shells. With or without string, cylinder shells are finished by wrapping in sheets of pasted paper. Enough is allowed so that it overhangs each end of the casing about one half to one shell diameter; the excess is torn into strips and smoothed down on the ends of the shell. Extra care is taken around the base of the time fuse to provide a good seal. Given shells of comparable size, stringless ones require more pastewrap than do the strung variety to produce casings of adequate strength, and consequently require more drying time.

A more refined style of cylinder shell building, perfected by Italian pyrotechnists in the nineteenth century, uses dry-rolled paper casings which are always reinforced with twine. Much of what will be said about these shells applies to the modern spiral can designs as well, but the traditional method is much more versatile and is particularly adapted to multiple breaks. A large proportion of the firework manufacturing companies in the United States were founded by Italian immigrants; among the best known are Rozzi, Grucci, Zambelli, and Santore, and there have been dozens of others over the years. For most of the twentieth century, a high percentage of cylinder shells was the norm in American displays. Increased regulatory burdens and labor costs, combined with the resultant deluge of Chinese imports, have made Italian-style shells less common today. However, some manufacturers never stopped using the traditional methods, and there are also hobbyists who specialize in quality cylinder shells. The essential techniques were described by di Maio[43] in 1891 and Domenico Antoni[8] in 1893, but few Americans have ever seen these references. Commercial makers clearly have no incentive to publicize what they tend to regard as "trade secrets," even when competitors are using very similar methods; the potentially dangerous nature of the product is another reason manufacturers have historically been reluctant to share their knowledge. A two-part article by Fulcanelli[46], published in 1984 and 1987, provides detailed how-to information for those who wish to make traditional cylinder shells. Other pieces in fireworks publications, while less comprehensive, also contain useful advice. Whether by design or through ignorance, most modern material on fireworks published in general-interest magazines either contains significant errors or is simply too vague to be of much practical use.

In Italian-style shells, the casings are initially quite thin; a general guideline is to use one turn of heavy kraft paper for each nominal inch of shell diameter. Case formers, usually made of wood or plastic, are sized to permit the finished shells to slide easily into the mortars. For example, a four-inch case can be made by rolling four turns of 70-pound kraft on a 3½" to 3⅝" former. Eight-inch shells are usually made on 7¼" formers, and ten-inch shells on 9" formers, to allow for the greater thicknesses of casing and pastewrap which become necessary with large shells. The casing requires no paste or glue, except on the edge of the last turn to keep it from unrolling. A kraft or chipboard disc is placed on the end of the former and the paper is folded down on it. A mallet or the end of a smaller former is used to set the folds; glue may be used to fix the casing to the disc, but many makers do not use it. The time fuse may be installed in the center of the disc, in which case the shell will be filled from the bottom. This method is necessary when the fuse has a flashbag attached, and may be convenient in some other instances as well. More commonly, a solid disc is used to close the bottom of the casing and the fused disc is added after filling. When empty, even a ten-inch Italian shell feels soft and insubstantial, and can easily be deformed with the thumb and forefinger. Ironically, the casing is less important to the strength of the finished shell than many other components. One or more turns of thin chipboard may be used to line the case, either by rolling on the former first, or by adding it after the case is removed from the former. The chipboard adds very little strength; it is not even customary to adjust the bursting charge when using it. It assists in filling shells to an even depth, and is also used to adjust the inside diameter for a more precise fit of shell components.

Shell contents are usually filled around a *canulle*, a tube of thin metal which is centered on the inside end disc. Canulles range from less than one inch in diameter for small shells up to three or four inches for twelve-inch shells. Traditionally, cut stars are the most common garnitures in Italian-style shells. If the stars are not too large in relation to the casings, they pack well and are not as inclined to shift or "flow" as round stars would be. Regardless of the other components used, the handmade coarse black powder called *polverone* is a staple in cylinder shell manufacture. While it certainly contributes to the burst gases, its primary function is to fill the interstices between stars and other components, making the shells very strong and solid when properly packed. To assist in the process, handfuls of stars and polverone are added alternately and the mixture is periodically consolidated with a simple tool such as a piece of wooden dowel. When the desired fill level is reached, the contents are leveled, adding more polverone if necessary. Ideally, single-break star shells are approximately "square:" a five-inch casing, which has an inside diameter of 4½ inches, should be filled about 4½ inches deep. Not surprisingly, commercial makers tend to underfill rather than overfill; some of them have turned out five- and six-inch shells that resemble oversized hockey pucks. The canulle is charged with powder, usually commercial FFA, and then carefully withdrawn to leave a central powder core in the shell. Sometimes finer powder such as FFFFA is used in small shells. Chlorate bursting charges, granulated like polverone, have been around for a long time but are not widely used in the United States today. Flashbags are a tradition in *spiderweb* shells, made with fast-burning charcoal streamers, and have become common in other shells where hard breaks are desired. The "bags" used are simply thin tubes rolled of kraft paper, tied onto the time fuses. They may contain either straight flash powder or a mixture of it with commercial black powder or rice hull powder. Adjustments must be made for each shell size and type; it is easy to use too much flash powder, resulting in an "overburst" shell, with many stars either not igniting or being completely destroyed. As an example, a four-inch spider needs about a quarter of an ounce of ordinary perchlorate flash powder; if nitrate flash powder is chosen, more will be required. When filling flashbag shells, no canulle is used, but polverone or a similar filler is still required between the stars. At the other extreme, a softer than usual burst can be obtained by omitting the commercial powder in the canulle and using straight polverone; this is suitable for willow breaks and for delicate inserts such as parachute flares.

Once a shell has been filled, an end disc (normally the fused one) is seated firmly on the contents and the protruding paper is folded down just as it was at the other end. With outside discs also in place, the shell is ready to be "spiked," or wound with twine (Photo 15-32). This important step is responsible for much of the shell's strength, as well as improving the symmetry of its burst if properly done. Almost any twine would offer some benefit, but experience favors certain types that are relatively thin for their strength and which absorb paste well. Most commonly used are eight- to twelve-ply unbraided cotton twines; the much stronger three-ply linen (flax) is popular among purists who are willing to pay the higher price. Both kinds are traditionally used doubled, with two strands running side by side and taken from two rolls. The reason for doing this (instead of simply using a single strand of larger twine) is that it doubles the strength while keeping the increase in shell diameter to a minimum. These considerations are especially important in large, elaborate multibreak shells, which may have intermediate pastewrappings as well as multiple spiking jobs. Not a few pyrotechnists have invested dozens of hours of work in a *pièce de résistance* only to find that the finished product will not fit in a standard-sized mortar. Some accomplished builders of large shells prefer to use *tripled* strands of two-ply flax, which is very thin and still stronger than most types of cotton twine. Besides producing minimal size increase, this technique spreads the reinforcement more evenly over the shell walls. Some makers prefer to work with dry string, but it is better to paste it before spiking; this allows it to stretch slightly and then to contract as it dries, as well as causing it to stick to the shell body rather than slipping. Tarred twine is also occasionally used. A convenient way to handle twine is to wind it on a "spiking horse" which has two upright arms, typically set two or three feet apart. The horse also serves as a convenient measuring device, and an experienced worker can easily calculate the amount of string for each shell so there is little waste. When enough is loaded onto the horse, it is painted or rubbed with paste until well saturated. The twine is tied to the base of the time fuse and the vertical spikings are applied first. When using multiple strands it is important to keep them parallel on the sides of the shell; any crossing of the string should be confined to the top or bottom where it will be insignificant. One otherwise reliable authority has stated that the string is advanced about ten degrees with each winding, but this method would be very awkward and would require end discs with markings to indicate the string positions. Normally, the shell is first divided into quarters with the string, which is much easier to judge without measuring, and also compresses the shell contents more evenly. Sets of two, three, or four passes, depending on the size of the shell, are applied at ninety degrees from each other. If the total number of vertical strings is a multiple of three, it will be necessary to allow for this at some point; otherwise the whole process can be accomplished by repeatedly halving the uncovered portions of the shell. The use of two or four passes each time this is done, so that strings do not cross exactly at the center, prevents excessive build-up on the top and bottom of the shell. The total amount used depends on the type of twine, the type of break desired, and the maker's priorities. Traditional guidelines call for sixteen vertical passes on a four-inch shell, two dozen on a five-inch, thirty-two on a six-inch, and so on, leaving the strings, or rather pairs of strings, about half an inch apart on all sizes. Circumferential or horizontal spiking is usually applied with similar spacing, so as to form little squares on the shell casing as though it were inside a tight-fitting net. Commercial makers may put as few as eight or twelve single strands of cotton twine on a five-inch "traditional" shell, especially if it contains a flashbag. At the other extreme, master pyrotechnists in Malta often completely cover shell casings with string, partly to compensate for the slower burning rates of their hand-made black powder bursting charges. Even when using the best commercial powders, traditionalists sometimes spike shells containing comets or pillbox stars more closely than usual to produce an especially hard, even burst; for example, they may use 48 vertical strings on a six-inch shell rather than the established 32[56]. Circumferential spiking may be varied at different points over a long shell, to allow for different components within.

Paste-wrapping follows the same rule of thumb as case rolling, *viz.*, one turn of heavy kraft is about right for each nominal inch of shell diameter. Long heavy multibreaks often need more, while single-break shells up to four- or five-inch caliber can be adequately pasted in with medium-weight paper, such as 40- or 50-pound, to expedite drying. Instead of being folded like the dry casing paper, the pasted paper overhanging the walls of the shell is torn into strips, which are then smoothed down carefully on the ends of the shell. Almost a full diameter of overlap should be allowed, at least on the final pasting. When more than four turns of paper are required, it is best to apply them in more than one installment, with time allowed for drying between pastewrappings, to keep the shell from remaining soggy for a long time. In such cases, the earlier pastewrap is often made to fold only partway across the ends, particularly on the top where excessive build-up around the time fuse can cause problems. In small shells and many types of report units, the paper may be smoothed and twisted around the fuses without tearing; this saves time with the thin paper used on such items, and forms good "crowns" around the fuses. If the paper is properly pasted and is rolled on reasonably snugly, the sides of cylinder shells tend to take care of themselves. Long shells which are lumpy or slightly crooked may appear hopelessly sloppy when the pastewrap is first applied, but will usually be hard and smooth after it dries. The grain of the paper should run the length of the shells, and of course, adequate drying time must be allowed. There is an alternative technique called *rinfasciature* (re-wrapping) which employs dry paper, with only the twine and sometimes a few final turns of thin paper being pasted. For details on this method, the reader is referred to Fulcanelli.[57]

One of the virtues of cylinder shells is that cylindrical garnitures of the appropriate sizes fit neatly into them. Sometimes, as in a small shell with whistles or serpents, the bottom of a long case may be completely packed with inserts, and a bursting charge and stars added on top. More commonly, garnitures are arranged around the periphery of a casing, leaving varying amounts of room for bursting powder in the center. Tourbillions, small color shells, and many types of report units produce their best effects when deployed in symmetrical rings. Ideally,

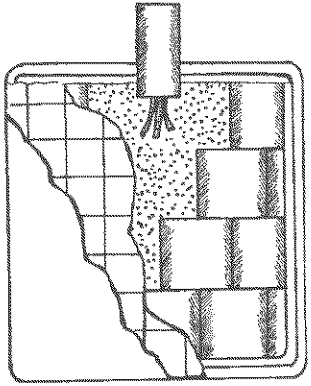
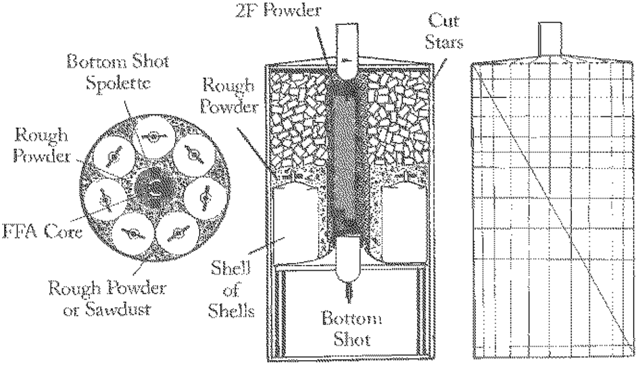


Figure 15-17. Comet shell (after Fulcanelli).[38]

cylindrical components should fit snugly enough that they do not fall out when the shell casing is inverted, even before other materials are added. In practice, it is not economical to have a multitude of slightly differing comet pumps and formers to give a perfect fit with each individual shell design. This is what makes chipboard liners especially valuable. Once a layer of components is in place, the spaces between the garnitures and the shell wall need to be filled, to eliminate air pockets and to strengthen the assembly. Polverone is often used for this purpose, especially with small tube items where it flows and packs well in the narrow interstices. Hardwood sawdust is more economical, especially with larger inserts, and wads of paper can also be used. Ordinary sawdust from pine or fir is spongy and troublesome to work with, while bran is avoided in most instances because it may encourage insects or mice to eat through the shell walls during protracted periods of storage. Depending on the size and type of shell, ordinary stars may be loaded inside the ring(s) of cylindrical devices, or the latter may occupy only part of the length of the shell and its other end may be filled completely to the walls with stars. In either case, the stars are interspersed with polverone, and a canulle is used to introduce a black powder core, just as in a plain color shell. Inserts placed near the top (fuse) end of a cylinder shell tend to be thrown farther from the center of the break. Apparently the top part of the casing has already begun to rupture before the burst powder at the bottom has completely combusted. This phenomenon is more pronounced in long shells and in those with bottom shots, and should be kept in mind when using different types and/or timings of inserts in the same casing. Such shells vary considerably in length and weight, but for obvious reasons, they are usually larger than plain star shells of the same caliber. On the other hand, a five- or six-inch shell containing a ring of tourbillions may legitimately be only 3½ inches tall and is not a case of deliberate skimping.

Comets of all types are well suited to cylinder shells (Fig. 15-17), especially as the shells become larger. Unless a shell is designed to produce a divided burst pattern, successive rings of comets are usually staggered so that when all are in place, the result suggests a circular brick wall. This is especially important with comets which are papered over one end, because it makes the layers fit together more neatly. The sizes chosen for a given effect depend on several parameters, much as described for chrysanthemum ball shells. Comets should be large enough to maximize a shell's burst spread, without there being so few that the break appears sparse. As an example, six-inch crossette shells may be made with 1¼-inch charcoal crossettes, four layers of ten. The same composition is used for 1½-inch crossettes to fit twelve per layer in eight-inch shells, and 1¾-inch crossettes to fit twelve per layer in ten-inch shells. Since tremalon (glitter) compositions generally burn more slowly than charcoal streamers, it is advisable to reduce the comet sizes when making tremalon crossette shells (Photo 15-33). Good performance is seen with 1¼-inch crossettes in eight-inch shells, and 1½-inch in ten-inch, requiring five rings of fifteen in each case. Thus a seemingly small decrease in size increases the comet count more than 50%, from 48 to 75. As with plain star shells, comet breaks are best when the heights and diameters are approximately equal. Hard breaks are desirable in most cases, and small- to medium-sized comet shells often have their centers completely filled with commercial grain powder. Shells of six-inch and larger calibers are often made using a canulle filled with FFA, either surrounded by straight polverone, or by small colored stars that give a contrasting center in the comet break. Cylindrical casings are bound to produce somewhat flattened or disc-like burst patterns instead of the perfect globes exhibited by Japanese shells, but the bursts of well-made comet shells in particular are very symmetrical. Indeed, hard-breaking shells with plain streamer comets are traditionally known as *sfera* (spheres). Gradual corruption of this word outside Italy is perhaps the origin of the term "spider," although breaks of charcoal cut stars with their delicate and somewhat irregular trails certainly bear a strong resemblance to spiderwebs. Good married comet shells with contrasting centers can easily be mistaken for double-petalled chrysanthemums; they lack the surprise color changes possible in the Japanese style, but have longer durations and may contain a greater variety of additional effects than are feasible in ball shells. With a suitable number of comets per ring, it is possible to make halved or quartered bursts of comets; indeed if the shell is large enough, the inner layer of colored stars may be sectioned as well.

Most of the foregoing remarks on comets also apply to pillbox stars, and to plain pumped stars of color compositions. The latter can be troublesome due to ignition concerns; priming each star on its ends only is extremely time-consuming, while rolling the stars in prime tends to make them irregular in shape, and might even be dangerous because of chlorate/sulfur friction when the finished stars are crammed into tight rings. Sometimes a shell casing is filled with layers of bare pumped stars (including sawdust or polverone – Photo 15-34), after



Top view **Cross-section** **Spiking Pattern**

Figure 15-18. Shell-of-shells with heavy report (after Fulcanelli)[illegible]

which the inside of the resulting "wall" is painted with slurry prime, dusted with meal powder, and allowed to dry. Even when a single-color break is made, cylinder shells over six-inch caliber rarely have cut or rolled stars as their only garniture. Tidy rows of cylindrical stars not only produce better effects, but add considerable strength to the finished shells.

In large cylinder shells, multiple concentric layers of comets are sometimes used. Unlike the comparable arrangement in ball shells, there is rarely a layer of burst powder between the two sizes of stars, although a small amount of polverone fills the interstices. Colored pumped stars, or occasionally large cut stars, work well when stacked inside a wall of streamer comets and primed as described above. In Malta and Italy, even explosive devices (*scoppietti* or *bombi*) are commonly loaded this way; an eight-inch shell may contain three concentric stacks of reports of different sizes and timings.

The *shell-of-shells* (Fig. 15-18) is a classic in the Italian tradition, and is one effect which is subject to more refinement in cylinder shells than in spherical ones. The miniature color shells employed are called *pupadelles*, which literally means "little dolls." The term strikes many people as humorous, but if these devices are hung up by their excess string to dry after being spiked, the resemblance to puppets is clear enough. They are made much like full-sized shells, although certain changes become necessary. Instead of being "square," pupadelles are commonly about 2½ inches long regardless of diameter. It is not feasible to core the burst powder in shells much under two inches in diameter; the usual procedure is to mix fine commercial grain powder with ¼-inch or smaller stars.

Large symmetrical breaks are not necessarily expected from pupadelles, preference being given to dense "splashes" of strong color. Where hard breaks *are* desired, flash powder or other energetic mixtures are sometimes added. Three inner and three outer turns of paper suffice for all sizes. Similarly, there is not much point in spiking with fewer than eight vertical strings, although single strands are adequate for these small casings. End discs are not always used, triangle or tongue folds being strong enough if the devices are properly filled. Chipboard or tagboard liners are commonly included to assist in making the pupadelles of consistent height. As a rule, timing is provided by ¼-inch cord fuse, which may either be cross-matched or simply primed on the ends. Spolettes are occasionally used for maximum precision in fancy shell designs. In very large shells, the "pupadelles" may be full-sized three-inch shells, or rarely even four-inch, and may themselves contain cylindrical inserts such as tourbillions.

One or more symmetrical rings of small color shells, often followed by a heavy report or a spider comet break, can be among the most impressive firework effects. It is especially important that the pupadelles fit correctly in the main shell casing, and that the various components are properly timed. It would be natural to assume that multiple concentric rings of small bursts are achieved by placing the pupadelles concentrically in a shell, but in practice this is never done. Such a design would not leave enough room for bursting powder, and would require inner shells so small as to be ineffective. Instead, successive timings of pupadelles are stacked much like comets, placing those with the longest timings at the top of the casing as described earlier. The bottom ring is placed in the casing with the time fuses up, a thick layer of polverone is poured on top, and the next layer of pupadelles is pressed down into the polverone with the fuses between those of the first layer. This technique is useful for all inserts that are end-fused, but solid

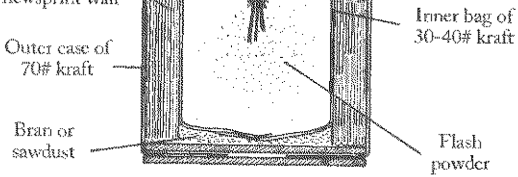
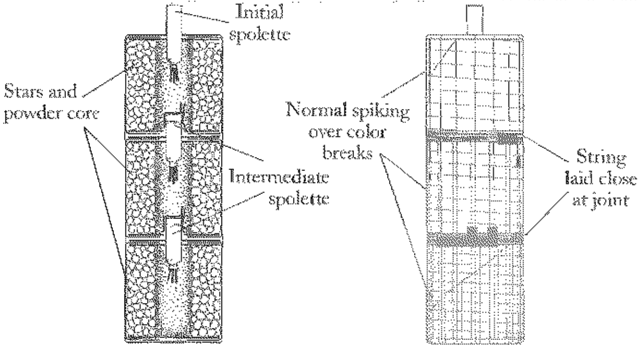


Figure 15-19. Hand-made report (after Fulcanelli).[36]

and even layers are particularly important in a shell-of-shells. Four or more rings of pupadelles may be used in large exhibition shells, which are made to order for special occasions (Photo 15-35). In commercial channels it is rare to see a shell-of-shells with more than one timing (Photo 15-36).

Salutes and other noise units play a major role in the Italian tradition; probably the most popular of all cylinder shells is the simple color break followed by one or more reports. Report casings may be hand-rolled from chipboard or a combination of chipboard and newspaper (Fig. 15-19), but today these techniques are little used except for large or odd sizes. Spiral-wound cores, with wall thickness ranging from ¼ inch to ½ inch or more, are available in the popular sizes. Thick end discs, or stacks of regular discs, can be quickly glued in place to make strong casings. Fusing, spiking, and pastewrapping are essentially the same as for star shells. Most salute mixtures do not require a great deal of confinement to produce strong explosions; well-made strong casings are important mainly as a safety measure.

When making a shell with a full-sized report, it is usual to roll the break casing directly on the report instead of using a separate former. The report must be completely finished and dried before beginning this step; if made with a spolette fuse the latter should be scraped clean and prepared by tying bare match over the exposed powder core (as seen on the report's spolette in Photo 15-34). If the report has a cord fuse it should of course be cross-matched. After a casing has been rolled on the report, it is often necessary to level the bottom of the report with a bit of sawdust and a disc, before folding or pleating the overhanging paper. A canulle can then be placed over the prepared fuse of the report (with care to avoid damaging the match) and the casing can be filled and closed like any other. Because of its position in the shell, a heavy report of this type is



Cross section **Spiking pattern**

Figure 15-20. Three-break color shell (after Fulcanelli).[88]

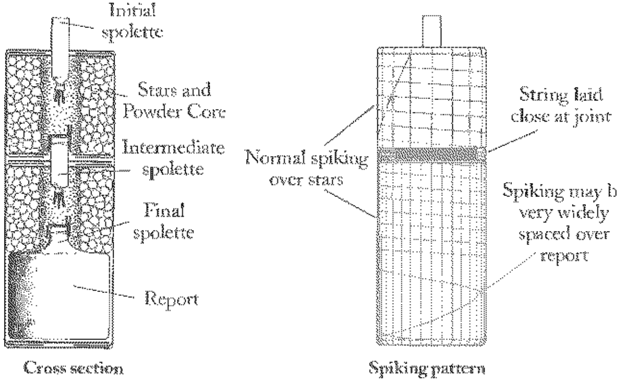
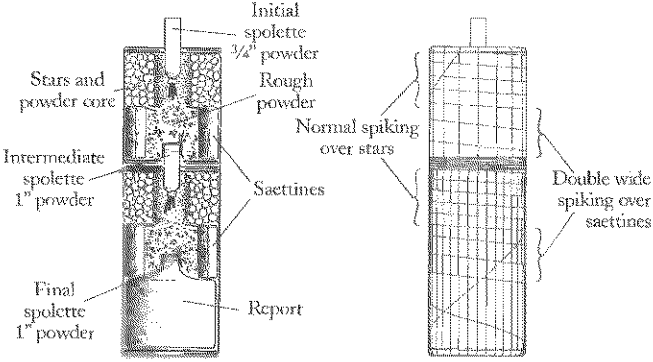


Figure 15-21. Two breaks of color and report (after Fulcanelli).[64]

commonly called a *bottom shot*; this term sometimes confuses people who have only casual contact with display fireworks, because they may assume it means the lifting charge. As shells become larger and casings thicker, allowance has to be made for paper buildup as mentioned earlier. For most purposes three-inch bottom shots can be built on 2½" diameter cores; the small increase in diameter when pastewrapping the reports will not be enough to cause trouble with the finished shells. The same cannot be said of six-inch bottom shots, which are best made from 5¼" casings rather than 5½". After complete spiking and pastewrapping, such reports will measure about 5½" outside diameter, making them ideal for rolling into casings for six-inch star or comet breaks. Commercial necessity and insurance regulations have made such concerns almost irrelevant in the United States today. Few five- or six-inch shells with bottom shots are sold, and those few are normally made in extra-long casings rolled on standard wooden formers. A smaller report is placed in the bottom of each casing and surrounded by firmly rammed sawdust, after which stars and other components are loaded in the usual manner. This cost-cutting measure suffices for most effects. Long, heavy, elaborate shells should be made with full-sized bottom shots, however. Not only do they make louder reports, but they are actually safer because they contribute great strength to the shells.

It is possible to make shells which produce sequential color breaks by a technique analogous to that just described. That is, the last break in the series can be made slightly undersized (intentionally), and the preceding break's casing then rolled directly onto it, and so on. This method has been widely used in parts of Europe, but requires many different sizes of end discs and other components, and

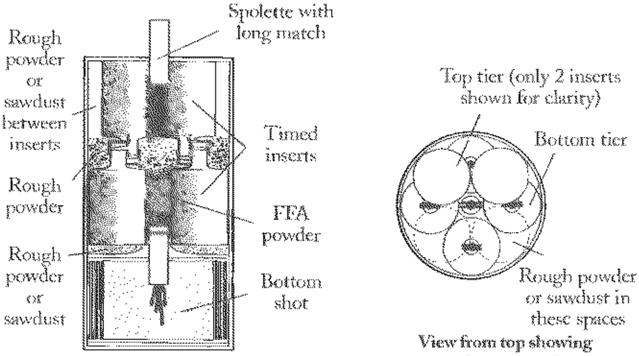


Cross section **Spiking pattern**

Figure 15-22. Two breaks of color and saettines with heavy report (after Fulcanelli).[69]

it is difficult to control the amount of paper which may remain on the shell at the end of the sequence. This can affect its burst adversely.

Usually, multi-break shells are made by joining a number of shorter casings of the same, or nearly the same diameter (Fig. 15-20). The final break (or break and report, Fig. 15-21 and Fig. 15-22) is assembled and closed just as it would be if it were to become a single-break shell, but using a shorter timing in its spolette, as appropriate. All the other breaks are made with bottom discs which have holes, because the time fuse of each break is ignited by the bursting charge of the previous one. There are many slight variations in technique, depending on the size and type of shell being made and the maker's personal preference. All the breaks may be filled individually, using plugs or paper "drumheads" to close the holes in the bottom discs until the breaks are joined. Alternatively, an empty casing, or one containing only rings of components around its periphery, can be set in place over the time fuse of the next break. Only then is the topmost break filled with bursting powder, fitted with its own fused disc, and closed. Most commonly, succeeding breaks are joined with vertical spiking only, and horizontal spiking is not added until all the breaks have been assembled. When full spiking is used on intermediate breaks, extra care must be taken to see that the shell's diameter remains as uniform as possible and that it does not become too large. Good six-inch shells of as many as five breaks can be made without using any pastewrap until after all five breaks are assembled. The strength of the contents, together with the pasted twine around each time fuse, are sufficient to protect each break from premature ignition. Such shells, however, are typically made with comets


Spolette with long match
Rough powder or sawdust between inserts
Timed inserts
Rough powder
FFA powder
Rough powder or sawdust
Bottom shot
Top tier (only 2 inserts shown for clarity)
Bottom tier
Rough powder or sawdust in these spaces

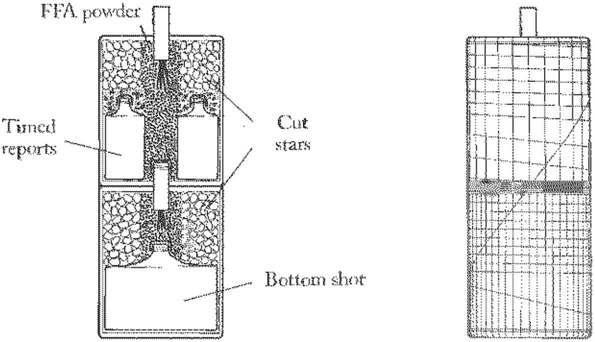
Cross section

View from top showing staggered position of inserts

Figure 15-23. Hammer shell (after Fulcanelli).

and need to be very carefully assembled; most others approaching the same size will benefit from two or three turns of thin pasted paper after the addition of each break. All the strength considerations mentioned in connection with single-break shells, such as choice of components, consolidation, and spiking, become much more important in multi-break designs (Photos 15-37 and 15-38). The number of possible variations is almost infinite, and detailed advice on their construction is beyond the scope of this book.

As a rule it is desirable for stars and comets to reach their full spread, and for other garnitures to finish their performances, before the next break of a shell opens – and particularly before a bottom shot explodes. Considerably more delay is required on the bottom shot of a shell containing whistles or tourbillions than that of a plain color and report shell. Larger shells have the advantage of longer flight times, and in shells with very long timing sequences it is often feasible to shorten the main time fuse so that the device begins its performance on the way up. In many cases compromises have to be made. With plain star breaks an ideal interval between bursts is about two seconds, but in long, small-caliber shells, experienced pyrotechnists may use spolettes with intervals of less than one second. The resultant breaks are invariably somewhat jumbled together, but this is better legally and æsthetically than having a shell hit the ground. Even among enthusiasts, shells having more than five or six breaks are rare, and tend to be regarded as stunts. From an artistic point of view, they usually do not repay the additional labor involved in making them, although there are certain exceptions. At one time it was not uncommon for Italo-American firms to include progressive series of multi-breaks in their displays. Such a sequence might begin with a



Cross section **Spiking pattern**

Figure 15-24. Draw-out shell (after Fulcanelli).[86]

four-inch color and report shell, then a two-break and report, and so on up to ten or more breaks. Another attractive effect is the "rainbow" shell, having seven or eight color breaks in the order of the visible spectrum, from red through blue or violet. In this case the arching trajectory and the running together of the colors do not detract from the effect. All such shells require extra-long mortars, are subjected to a great deal of stress on firing, and are never quite so reliable as shells of more balanced dimensions. One sometimes hears that it was electrical firing that killed off the multi-break shell, but history does not really support this view. Ignition from a battery or a magneto has been a practical option for more than a century. Furthermore, there are other ways to achieve precise timings or to put a lot of material in the air at once. Even the most traditional pyrotechnist rarely has reason to make – for example – a three-inch ten-break shell. Instead, he might more usually place ten three-inch inserts, with suitable timings, inside an eight-inch casing. Such a shell is more trustworthy and goes higher than a three-inch "salami," and the design permits more options, such as an additional eight-inch comet break.

Timed shell inserts typically have their fuses graduated in quarter-inch steps, with a slightly longer interval before the final break or report. This construction permits certain effects that would not be feasible with sequential ignition of each break. For example, spiderweb shells, especially small ones, are commonly made with flash bags, the explosions of which would probably damage or fail to ignite any secondary time fuses exposed to them. By having many fuses ignite from the same primary shell burst, there may be a series of timed spiders, often with the last one substantially larger than the others. The technique is more commonly applied to reports, and there are many variations on the theme. The construction resembles that of the shell-of-shells, except that report units are usually larger and fewer in number in a given size shell. Timed shots are sometimes called *rondelles*, which implies that they explode in a circular pattern (Photo 15-39); in practice, makers do not worry as much about this refinement with noise units as they do with other types of inserts. Often there are only four shots in a layer, with little room for bursting powder between them. This does not "draw" a very impressive circle upon opening. It is convenient to make such shells with the smaller reports seated firmly atop the bottom shot, with any colored stars or additional effects placed on top of the reports. Shells containing only timed reports are also quite popular, and often contain two layers of smaller ones. The *hammer shell*, analogous in construction, is a traditional favorite (Fig. 15-23). What few are seen today usually feature small color breaks alternating with reports, the final effect being a heavy report. Another classic style employs alternating flash and dark reports. In either case, the two types of inserts make different noises when they explode, sounding something like an echo. Specifically, they mimic the sound made by a blacksmith's hammer when he bounces it on the anvil in alternation with blows delivered to his work-piece.

A related timed effect is the *draw-out* shell (Fig. 15-24), a term which is sometimes applied in a haphazard way to almost any shell containing both color and timed shots. One defunct maker's price list shows a "hammer draw-out," and it is uncertain whether this meant a choice between the two, or a hybrid device, or whether the makers were not even certain what it was and were trying to cover all possibilities. While it is difficult to buy a true draw-out shell in the United States today, the term does have an established meaning. The first break contains four timed reports (optionally accompanied by stars), *and is followed by another full-sized shell break*, then by a bottom shot. The second break is normally one of plain colored stars but it may contain almost anything, from fancy comets to pupadelles, or even a barrage of smaller noise units such as saettines. The originator of this design remains obscure, but with the benefit of hindsight, the curious name fits. The shell may be viewed as one of the most popular traditional shells, color and five timed reports, which has been extended or "drawn out" by the addition of a surprise effect.

Sun and planets is another classical term that may mean different things to different people. Simply placing good streamer or tremalon stars in the center of a shell-of-shells can produce an attractive effect. However, a more refined version uses only pupadelles and burst powder in the first break, followed by a full-sized star or comet break and often a bottom shot. This is a peculiar multibreak, in that the second break opens before the components from the first break have become visible. The pupadelles have time to achieve a large and symmetrical spread, after which the "sun" makes its appearance and the pupadelles burst.

Practically all the pyrotechnic effects discussed in this chapter, and a few others as well, may be included in a properly made cylinder shell. It would be wrong to downplay the ingenuity involved in making a good multi-petalled *warimono*, but some feel that there are few firework questions that cannot be answered by skillful application of the case-former. Indeed, multiple fancy ball shells may be used inside a cylinder, if the latter be large enough. It is not only because of economic changes that elaborate cylinder shells have become less common; some other considerations will be mentioned in connection with firing displays. However, large shells do not merely consume more material than their smaller counterparts; they require considerably more labor as well. Seemingly minor details become more troublesome; pleating the paper down smoothly onto the end disc of a twelve-inch shell takes the better part of half an hour, whereas folding it on a six-inch is the work of a few seconds. Crossettes and other specialized comets may need additional pastewrap to withstand a hard break in a ten- or twelve-inch shell. Other changes are not as subtle: handling a forty-pound shell for an hour or so while spiking it is enough to tax the endurance of most workers. Bigger is only better when the quality is kept up to par and the design is intelligently chosen.

Even in Italy one cannot assume that every fireworks display will feature large fancy multi-breaks, although they are still common in the southern part of that country, and especially so on the nearby island nation of Malta. The latter is almost entirely Roman Catholic; many of the people speak Italian in addition to their own unique language, Malti. Many of the cultural traditions are the same as in southern Italy, particularly the association of fireworks with religious observances. In this relatively isolated circumstance, there has been little incentive to change old and proven techniques, except to maximize the performance with whatever materials are at hand. Many European cities and villages hold their main annual display on the feast day of the town's patron saint. In Malta especially, many of the pyrotechnists work at other jobs for financial gain and make the fireworks in their spare time. The displays are seen as a mixture of religious duty and civic pride, with each village vying to put on a better show than its neighbor. It is not uncommon to see dozens of six- and eight-inch multibreaks stacked up like cordwood (Photo 15-40).

In the United States, the situation is quite different. Except for the ubiquitous three-inch salute, perhaps less than five percent of shells fired in modern displays are cylindrical. Most of these are single-break, and a lot of them are made with various hybrid techniques adopted to save time. Round stars are now common in cylinder shells, as are rice-hull bursting powders of the type described under ball shells. While these have the potential to produce some appealing effects, many are not particularly well made and have done little to challenge the ascendancy of the imported ball shell. Aesthetically dubious combinations are common, such as a willow break with a heavy report. There is a tendency to try to make complex effects in shells which are too small to show them well. One large domestic manufacturer, which ceased operations in 1997, used only one size of pupadelle for its entire line. The effect was not bad in five- and six-inch shells when all the inserts ignited, but the company insisted on selling a four-inch shell-of-shells containing only four inserts. The result was unimpressive to say the least, and because of the labor cost involved, the price charged could have bought two or three good Chinese chrysanthemums of the same caliber. Relatively few six-inch cylinder shells are offered today, while commercial eights are very scarce and are not even listed by most wholesalers. However, several small manufacturers, and two or three large ones, keep the tradition of good cylinder shells alive.

Lifting Charges and Leaders

High-grade ball shells from Japan and Taiwan are sometimes offered without lifting charges. While this option has its advantages, it can cause a great deal of consternation if the shells are delivered by mistake to a fire department or community service club on the third of July! Attaching a lift charge is a rather simple and straightforward procedure, although it becomes more time-consuming when the time fuse is at the top of the shell.

With a few exceptions, a ball shell will have its delay fuse at the bottom, embedded in the lifting powder. The leader is simply a piece of piped match, which passes through the suspension loop at the top, around the shell, and to the time fuse, where it is bared at the end and fixed in place. Various kinds of paper or plastic containers can be used to hold the lifting charge; when ball shells were commonly made in Europe, it was usual to employ stout cardboard cones. The mortars used with such shells had conical cavities in their breech plugs, the idea being that as successive shells were fired, the leftover cones would stack neatly together instead of leaving bulky debris that could cause trouble with reloading. A good method, not requiring any special materials or formers, is simply to cut a slit in the middle of a square of paper and glue it over the prepared time fuse, leader and all. The lifting powder is then poured into the center of the paper, which is gathered in and tied to form a sort of "bun." After cutting off any excess, the lift pouch can be pressed down gently against the shell to flatten it a little. Finally, a sheet of strong paper is pasted over the entire bottom part of the shell, taking care to see that it is rubbed down smoothly over the leader and is allowed to dry well before the shell is picked up. Use of paste instead of glue, or worse, plastic tape, for lift wrap, not only gives a better finish, it reduces the amount of smouldering debris left in the mortar when the shell fires.

Cylinder shells, especially those made with spolettes, customarily have the time fuses at the top to protect them from the pressure of the lifting charge. Small single-breaks with machine-made fuses are often finished with their fuses in the lift to save time. Shells of three or more breaks can certainly be made the same way, but most pyrotechnists prefer to have the extra safety margin where high pressures are generated. Even Japanese ball shells are usually top-fused in the giant sizes. There are slightly different methods of lifting cylinder shells, but the first step is to attach a "passfire" to the time fuse and run it around the shell to the bottom. Normally, this consists of two strands of good match in a piece of tough paper pipe, although for small single-break shells, the piping is sometimes omitted. The use of doubled strands makes it almost impossible to "choke off the fire" when tying knots around the match. Paper, which is best pasted, can now be rolled around both shell and passfire. For commercial shells of ordinary size, the paper is often cut wide enough to project over both ends, and is tied shut over the powder at the bottom. A neater finish is made by pasting on only a thin "lift bag" at the bottom, folding it in and covering it with a pasted patch as described for a ball shell. The sides of the shell can then be covered by another strip of paper, often colored or patterned. Ordinary bundle match is sometimes used for leaders, but stronger hand-rolled pipe is a better choice. At the end tied into the shell, an extra piece of bare match is usually inserted. On a shell with machine-made time fuse, the leader can be attached to the fuse, and the overhanging paper left for the purpose can then be cinched in and tied around the leader. For spolettes, it is usual to roll a "bucket," simply a few turns of kraft made into a ¾" to 1" diameter tube. The bucket is tied (and often glued for good measure) over the spolette and its attached passfire, and the leader is tied into the top of the bucket.

Shells for commercial sale have the lighting ends of their leaders bared for a few inches and the exposed match covered with colored safety caps. Some Chinese shells have a short piece of "safety" fuse attached at this point with the idea of giving the people igniting them more time to get away, but the delays are so variable that any gain in safety is doubtful. Shells destined for electrical firing may of course be made without leaders, placing electric igniters directly in the lifting charges, or, in the case of a top-fused shell, in the bucket. In practice, most makers do not have too much control over the use of their products, and the problems often encountered with electrical firing systems also make it a good idea to have an ordinary leader fuse as a backup.

A popular rule of thumb says that a shell should rise about a hundred feet, or a bit more, for every inch diameter. While this may sound simple-minded, it holds true for most kinds on the market. Some makers deliberately skimp on lifting powder, not only out of simple stinginess, but because in places with limited space, such as city parks, low-breaking shells appear larger to the spectators and are less likely to drift into unsafe areas. In most cases, the traditional altitudes are to be preferred. The amount of commercial black powder needed to lift a shell varies from about five to ten percent of the shell's weight, depending on several factors. The fit of the shell in the mortar obviously makes a difference, but within normal limits, it is not as significant as one might expect. An extreme gap, as when a shell designed for a five-inch mortar is accidentally loaded in a six, will cause the shell to burst on or near the ground. However, it is rare to find commercial shells undersized enough to cause any problems with the designated sizes of mortars. Shells of normal size will reach good altitudes using one ounce of FFA powder for every pound of shell weight. Many experienced pyrotechnists like to sift the powder through an 8-mesh screen and use the "fines" for ball shells and small cylinders such as three-inch finale shells, reserving the coarse fraction for heavier cylinders. Chinese shells are normally lifted with powders of finer granulations, which resemble American black sporting powders or FFFFA but are usually less energetic. Ball shells are much lighter than cylinders of the same diameter, and their shape theoretically makes them more resistant to crushing. Even so, many people feel that the use of excessively fast lifting powder contributes to the relatively high incidence of mortar bursts experienced with imported shells of six-inch and larger sizes. These things should be borne in mind if one has to deal with shells which have had their lifting charges damaged or torn away in handling. There is a "cannon" grade of black powder, comparable to FFA, which is packaged for retail sale in one-pound cans, but most sporting goods stores do not carry it. If it is necessary to use Fg gunpowder, extra care should be taken and the minimum calculated lifting charge should be tried first. If there is any doubt about the appropriate amount, or if the time fuse may have been damaged, the shell should be returned to the seller.

Good hand-rolled leaders are strong enough to support shells up to ten pounds or so as they are lowered into the mortars. Heavier shells require some sort of lowering cord, which in the case of ball shells may simply be tied to the loop of rope on the top of the casing. Cylinder shells are not quite as easy to deal with, but moderately heavy ones using spolettes may have the cord tied to the base of the spolette, taking care to secure the knot so it cannot slip and damage the passfire. A cylinder shell exceeding twenty pounds is best equipped with several cords passing completely around the bottom and back up to the top where they are tied together. This step is normally performed before the lifting powder and finishing wrap are added, so that the cords are held smoothly in place.

Aquatic Fireworks

At one time, pyrotechnists, like the United States Marine Corps, were expected to make use of their skills in the air, on land, and on water. Because water fireworks are practically a thing of the past in western nations, they will receive only brief notice here. Most of them can readily be imagined from devices already described; for example, there were various types of wheels designed to float on the surface of a pond or lake. Perhaps the most distinctive and popular of aquatic fireworks were water rockets, with such names as "fish" or "diving devils." Some of these devices merely skimmed about on the surface, but the more ambitious type of water rocket was designed to dive and resurface multiple times. This required careful waterproofing and balancing. Layers of powerful driving composition alternated with a special mixture which gave a shower of sparks at the surface, but did not produce enough thrust to force the rockets under. Often the nose of such a device was fitted with an angled or curved piece which caused the rocket to resurface in different places, instead of merely bobbing up and down. "Barrils de trompes," consisting of batteries of large-bore sequentially-firing mines (not unlike today's exhibition candles made with felt wads, *q.v.*) were placed inside waterproofed and ballasted containers so as to float with their muzzles just above water, repeatedly discharging their garnitures like a submarine volcanic eruption. Examples are illustrated in Fig. 15-25.

Into the Victorian era, aquatic fireworks were seen at most displays where suitable bodies of water were available. On the Prince of Wales's tour of India in 1876, there were many fireworks displays, including a memorable one at Trichinopoly; "in the tank below the rock were innumerable water fireworks...the lake

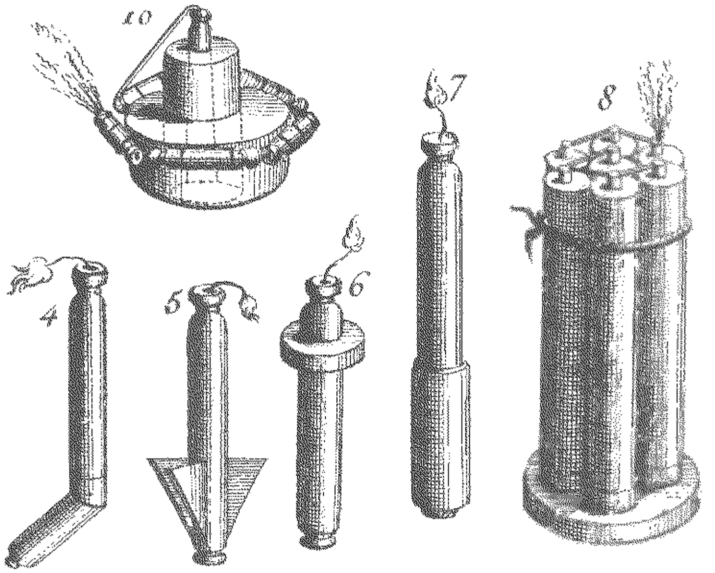


Figure 15-25. Water fireworks (after Perrinet-d'Orval, 1750)[187]

being alive with fire devices of every hue."[26] Minimal fire danger was one obvious advantage of this class, but there were occasional mishaps. J. T. Desaguliers witnessed a display on the Thames in the early eighteenth century in which a diving devil exploded underneath a barge.[149] The report contained "much less than an ounce" of gunpowder, but due to the incompressible nature of water the bottom of the vessel gave way, dumping all the passengers into the river. However, fireworks designed specifically for use in water fell out of fashion long before the modern-day explosion in lawsuits. Most of the items were not easy to enjoy from a long distance, and were more suitable for small fêtes than the giant spectacles of today. It is worth noting that the use, now much revived, of pyrotechnics on the stage (discussed briefly in Chapter 14) was as moribund fifty years ago as water fireworks are at the time of this writing. There are signs of a minor revival of interest in aquatic fireworks.

The Japanese have a type of serpent mine called "goldfish" (*kingyo*) which is fired horizontally over water so that the inserts "swim" around on the surface. This item demonstrates the fundamental simplicity of fireworks – it exemplifies an uniquely eastern approach to the same item found in the West as the mine of serpents. Tubes of an adequate wall thickness are closed off at one end and then charged with a driving composition. The open ends are closed with a drumhead of paper and then primed. These are, of course, equivalent to unchoked serpents (*q.v.*). A "lifting" charge (here, the purpose is not so much to *lift* them into the air, but merely to propel them) is made by containing FFFFA black powder between two rounds of tissue paper – very much in the manner of a round teabag. A stiff case is closed with a wooden plug or paper disk, punched to accept

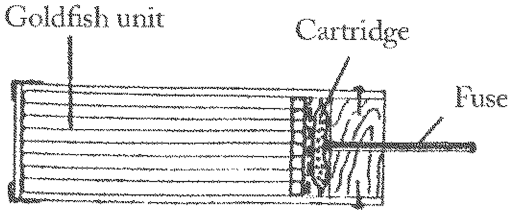


Figure 15-26. Goldfish assembled (after Shimizu)[216]

a piece of time fuse; the fuse and powder sack are loaded, and the case filled with the little serpents (loaded primed end towards the blowing charge). Several thicknesses of paper – *i.e.*, thick enough to withstand being in the water for ten seconds, but not so strong that the end plug is preferentially blown out – are used to close off the piece. Fig. 15-26 illustrates. *Goldfish* is a specialized item today; nearly all manufacturers make star shells, whereas a few produce this kind of "signature" product and sell it to the rest of the display industry. In the old days, many manufacturers had ball mills or stamp mills for producing their own powder, but economics and the desire to abandon all unnecessary hazardous operations have meant that black powder is purchased. Similarly, the driving composition for these serpents has been a relatively slow burning powder which has been milled and granulated to improve performance for this specific application. Shimizu describes use of a ball milled powder as well as giving precise receipts and measurements for a specific size of product. The reader should consult this reference[216] for more details.

Another Japanese practice is better characterized as a feat of daring and *sang-froid* than a case of specialized pyrotechnic engineering. A warimono-style shell without a lifting charge is ignited and thrown out of a small boat, after which the occupants row madly to escape the flying stars. The appearance of the shell is of a colored sun half risen on the horizon, with a more dull reflection of the lights in the water (Photo 15-41). This is a popular firework effect for shows given near a lake or river. The shells are made specifically for this purpose using a piece of time fuse of greater length than normal, and employing polystyrene hemispheres glued in place around the shell to provide buoyancy.

The venerable French firm of Lacroix-Ruggieri makes a variety of aquatic effects resembling those illustrated in the old books, as do some of the Spanish manufacturers. Many of these are loaded as garnitures into mines, which are intended to be fired from mortars angled at low elevation over the water, into which they fall and exhibit their various effects. One development showing the application of recent technology is the so-called "water shell," in fact, a six-inch mine containing nine approximately three-inch plastic shells fitted with long time fuses. After firing, these float in the water until they explode at different intervals according to their respective timings. Such products have been seen occasionally at large displays fired over water in the United States, but the difficulty of keeping unauthorized boats out of the display area, and the resultant potential liability, probably will limit their future use.

Display Operation

In some respects, setting up for a typical public display is less complicated than it was in the eighteenth century, with its large fancy set pieces, flights of skyrockets, and water fireworks. In most industrialized nations today, the emphasis is on large volumes of shells, with Roman candles and other low-level effects playing a secondary rôle. Lancework is still done, but is not a significant part of the typical public display. In the United States, lancework pieces are more likely to be encountered at private parties or in corporate events and advertising. The firing of large, choreographed shows is obviously a specialized endeavor, and those involved in it are already too aware of the issues affecting their specific localities. At the same time, thousands of smaller displays are fired annually all over the United States by volunteer fire departments and by community organizations such as the Lions' Club, Rotary, or Jaycees. It is to be hoped that these parties may find the following observations useful.

Mortars are best made five or six times as long as their internal diameters, in the common sizes, and can be a little shorter in large calibers. For most applications, there is no point in having a twelve-inch mortar six feet long, and such a thing is difficult to handle. Long mortars do make slightly more efficient use of lifting powder, but if the standard lengths are exceeded, many commercial shell leaders will fail to project far enough from the muzzles and may slip inside where they cannot safely be ignited.

Whether or not the metric system has been adopted in the country of origin, shells will generally be found to conform to standard sizes in inches unless they happen to be made in an indigenous system of measurement (such as the Japanese *go**). The standard sizes are 3", 4", 5", 6", 8", 10", and 12". Seven-inch Chinese shells are occasionally seen in the United States, but neither plastic mortars nor steel pipe are easy to obtain in this size. Salutes of 2" and 2½" calibers are often used in display work in pre-loaded finale boxes, but these sizes are rarely sold as individual shells. Mortars over 12" are rarely used and are essentially custom projects, although 16" and 24" ball shells are sold in the United States, and 16" plastic mortars are available.

In American fireworks business usage, there was formerly a custom of describing shells by circumference rather than diameter, or at least such was the

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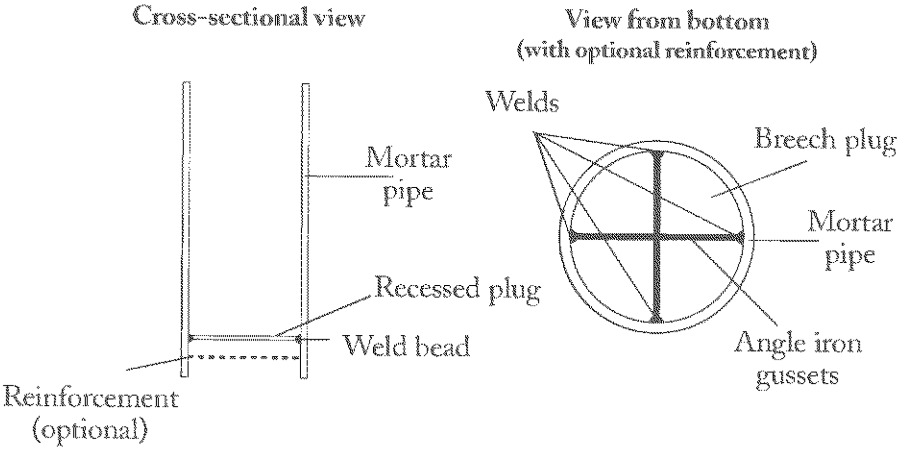
* The Japanese use a native measuring system for their shells denominated in units called *go* – a little larger than an inch. The smallest shell is 2.5 *go* – the equivalent of our 3". The Japanese domestic 3 *go* is not exported, it being equivalent to a 3.5" shell, and 4" shells are made only for export. In practice, from 4 *go* through 7 *go*, one may simply add 1 and refer to the size in inches. One *shaku* is equivalent to 10 *go*, but this measurement is used for the largest shells only: a 10 *go* shell (famous to those who have seen Japanese displays with an announcer shouting out "*ju-go tama!*") is the same as our 12" shell, but a 24" shell is referred to as a *ni shaku tama*, and so on.



Cross-sectional view

View from bottom (with optional reinforcement)

Fig. 15-27. Steel mortar construction

justification advanced for calling a 3" shell a 9", a 4" shell a 12", *et cetera*. This regrettable practice seems to have been an instance of commercial puffery, and has largely been abandoned, though old stock may still be found bearing such misleading labels.

Steel mortars are the traditional choice; the preferred material is American Nationals Standards Institute (A.N.S.I.) Schedule 40, or equivalent seamless drawn-over-mandrel pipe. Odd lengths of scrap pipe or well casing offer the attractions of considerable economy as compared to new material, but should be accepted only if their inside diameters do not exceed the nominal diameter desired by more than ⅛" if the latter is 8" or under, or by more than ¼" if 10" or greater. In any event, the inside diameter should never be less than the nominal diameter. In addition, the pipe ought not be accepted should it have excessive rust pitting sufficient to weaken it or to cause shells to snag on a rough surface as they are lowered into the mortar. Seamed pipes are suggested by some authorities[216] as offering a known point of weakness that can be oriented away from the audience and crew, should a mortar give way during the course of a display. Customary American practice disapproves of seamed pipe and demands the seamless variety.

Steel plate, usually at least ¼" thick, and thicker for larger-size mortars, is used to seal the breech ends. A simple expedient is to cut square plates and weld them to one end of the length of pipe around the outside. Such mortars are sometimes used on barges or in above-ground boxes where they are ballasted with sand; the end plate keeps them upright and prevents them from moving. However, when the mortars are buried in the earth in the more usual manner, this arrangement makes them more difficult to remove without digging. The preferred method is to cut the plugs round, turning them on a lathe so they fit snugly inside the pipe. If using a thick plug, it is sometimes chamfered on the underside to provide for a better weld. The plug is then recessed a short way into the bottom of the pipe and welded in place around its entire circumference. The temptation should be resisted simply to "tack" the plug in place with a few spots of welding. Admittedly, the breech pressures generated by most shells are very low, and such mortars often withstand many firings. However, the time usually comes when a long, heavy, and expensive shell is loaded, or when rust takes its toll on the stingy bits of welding rod alloy. Then the bottom comes out of the mortar, and the shell bursts low or on the ground. A proper weld bead run all the way around the joint takes full advantage of the strength of steel. Mortars specially made for heavy shells often have reinforcing gussets of angle iron welded across the recessed breech plug for further strength. Mortars made in the recommended manner will last indefinitely if kept reasonably clean and dry. Fig. 15-27 illustrates these methods of mortar breeching.

Most types of shells can burst in a steel gun without damaging it; even when a long multi-break collapses, the bottom shot usually makes it out of the gun before exploding. Salutes are the one type of shell which ought not be fired from steel because of the possibility of shredding it into fragments that travel with sufficient speed to wound or kill. Large chrysanthemum style shells may also be powerful enough to destroy a steel mortar from a premature burst. The danger from metal mortars (and other types as well) can be kept to a minimum by adhering to the standard procedure of burying them in the ground, so that only a few inches of the muzzles protrude above the surface. A timber may be placed below the mortars, to prevent their being driven below ground level by the recoil from repeated firing. The main disadvantage of steel mortars is their weight, especially in large calibers. Handles are sometimes welded near the mouths of the latter to make it easier to remove them from the earth. A few display operators use lightweight, seamless steel tubing of a special alloy, but this material is expensive and not easy to find. Aluminum mortars have been tried but are certainly not common.

Paper mortars have long been used as a lightweight, low-cost option, especially for finale racks, and anywhere that large numbers of salutes are to be fired. Three- and four-inch are the common sizes, although larger ones are sometimes available. While good parallel-wound tubes would be preferable because of their strength, practically all commercial paper tubes in such sizes are spiral-wound. The exposed "seams" in the bore of such a mortar are vulnerable to charring and unravelling; mortar life can be extended by treatment with varnish or phenolic resin. Paper mortars are usually breeched with turned wooden plugs, which should be both glued and nailed in place.

Plastic mortars are increasingly used today because they are more weather-resistant and usually last longer than paper. Even shooters who prefer steel for general use often buy plastic in eight-inch and larger sizes, because they intend to use them only for ball shells and the mortars are so much easier to carry than steel. One-piece plastic guns are available in the smaller sizes, but some, alarmingly, are thinnest just ahead of the breech, where they need to be the strongest. Most of the plastic mortars in use are plugged with the standard wooden plugs originally marketed for paper mortars. The tube material of choice is high-density polyethylene, or "HDPE." The more commonly available PVC pipe should

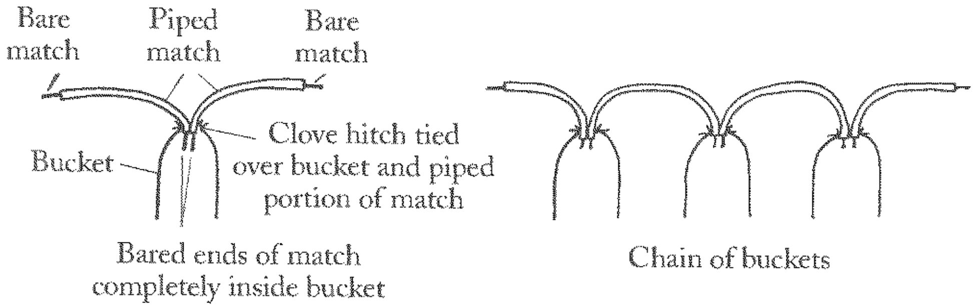

Bare match
Piped match
Bare match
Clove hitch tied over bucket and piped portion of match
Bucket
Bared ends of match completely inside bucket
Chain of buckets

Figure 15-28. Bucket chains (after Fulcanelli).[86]

never be used, because it is relatively brittle and easily blown apart into sharp fragments.

There are two basic approaches to firing quantities of shells. One is to pre-load each device in its own individual mortar before the display begins. This method is essential for finale chains or electrically-fired sequences, and there are some who feel it should be used for all display work. Pre-loading is certainly not a new idea, and a hand-fired show of this type is perhaps the most reliable of all options. In the past, it was not uncommon for a firework company to set up a "one-match" display. That is, all the shells, and groups of shells, were connected by spolettes or Bickford-type delay fuses in a sequence which might last as much as half an hour. Such practices are rare today, and when shells are "chained" together, it is usually done to fire them in rapid succession.

Finales or smaller flights of shells to be fired in this fashion may be fused together by a variety of techniques, the most common of which employs piped match connected by "buckets," or thin paper tubes consisting of two or three turns of light-weight paper, *e.g.*, 30-pound kraft, ⅝" to ¾" in diameter and about 3" long. Lengths of piped match varying in length from perhaps 10" to 18", and having 1" to 1½" of match bared on either end, are assembled by tying with clove hitches into successive buckets, forming the chain. It is preferable to use strong, hand-rolled match pipe and stout quickmatch for this purpose, since chains typically receive somewhat rough handling on the display site, and also because it is

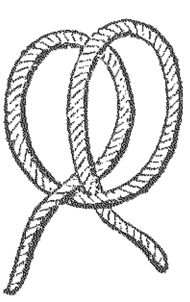


Fig. 15-29. Clove hitch.

preferable for the chain to be strong (so as not to break) and the shell leaders to be relatively weak (so they break away after having served their purposes). However, in expedient situations, continuously-entubed "bundle match" is often used, the piping being torn or cut partway through at intervals, exposing the match without severing it. At each cut, the match may be bent double and tied into a paper bucket – which of course may be hand-rolled, although a common practice is to use the paper coin wrappers cheaply available from stationers. Such practice is not the most workmanlike, but frequently serves for last-minute work at a display site.

When the requisite number of chains (Fig. 15-28) is made, the shell leaders can be tied into them in the desired order. It is important to use clove hitches (the traditional tight knot used in fireworks – see Fig. 15-29) and to see that they are snug enough to prevent slipping. Additional knots are sometimes tied around the match between each bucket to slow the timing, but the results of this are quite variable depending on the match used. An auxiliary length of pipe, for relighting in the event of a break in the chain, may be tied in at several intervals along the finale, bared and capped like a shell leader. Shells are often chained in advance and in this case, the number in each chain should match the number of mortars per rack, usually no more than ten or twelve. This is much better than trying to handle a chain of a hundred shells, and the shorter chains can be quickly tied together at the display site. After a chain of shells is loaded into its mortars, it is a good idea to anchor the festooning loops of match by tying or by other methods to the tubes or the rack. This makes it less likely that a departing shell will damage the chain or pull a neighboring shell out of its mortar.

Burying large numbers of mortars is laborious, and in many places, such as barges, carefully tended grounds, and paved areas, it is not possible. Racks are securely staked or tethered to prevent them from tipping over. Large single mortars are sometimes placed in barrels or boxes filled with sand (Photo 15-42), to add stability and perhaps offer some protection if a powerful shell bursts in the gun. There is still potential hazard from muzzle breaks and shells coming back down, but today, most of the danger is to the shooters rather than the spectators. Display insurance policies are often made conditional upon observance of separation distances as set in N.F.P.A. Standard 1123, and in some cases distances are prescribed by state laws. The minimum viewing distances are generally reasonable, ranging from a few hundred feet to a quarter mile, and it is not a bad idea to follow them, even where it is not legally required. More controversial N.F.P.A. guidelines include recent recommendations on electrical firing, specifically the rule that all shells larger than six inches must be ignited in this manner. Certainly, the rule was inspired by real problems with large, cheap chrysanthemum and peony shells, which are more potentially destructive than most other kinds, especially when fired in close quarters such as barges. However, many people falsely assume this restriction is a federal law, and do not bother to question its validity in other circumstances. There are even individuals pushing for mandatory electrical firing of all display material, but many of these people stand to profit from selling firing panels, electric igniters, or plastic mortars. At the time of this writing, the N.F.P.A.-1123 guidelines are under review, and nothing further will be said about them here.

As in many other endeavors, the basic term "electric" is often confused with the term "electronic." Electrical firing may be done with a firing panel or even a handheld switchbox, using a storage battery as a power source. This allows one operator to control a large number of shells, with good timing and without being too close to the mortars. In displays where only a few shells are to be fired by electricity, even a switchbox is not really necessary. One may simply touch the lead wires to the terminals of a battery, or use a blasting machine which generates its own current. The heavy T-handle kind made famous in cartoons and movies is much more powerful than necessary, and many shooters prefer the small handheld version with a twist handle, or the more recent capacitor-discharge variety. Electric matches ("squibs" to many fireworks men, though not strictly speaking a correct usage) now cost in excess of fifty cents apiece. Fireworks wholesalers selling small "ship" shows may include a number of them if requested when a display package is sold. With larger displays, where hundreds or even thousands of shells are to be fired electrically, cost becomes a significant factor, as does complexity of wiring. Because each additional circuit presents another opportunity for failure, it is considered good practice to combine electric firing with the use of pyrotechnic delays and chaining in order to reduce the number of firing "cues." Many very ambitious displays have been fired, through the use of such techniques, using fewer than one hundred electric matches.

True electronic firing is also possible, using pre-set timing devices: specifically, computers are increasingly used in connection with recorded music to produce "choreographed" displays. In order to make a shell burst coincide with a specific beat of music, it is necessary to know the rise time of each individual kind of shell being used. Naturally, this requires dependable supplies of very consistent material and is more feasible for large operators than smaller ones. In a few cases electronic delays within the shells have been substituted for pyrotechnic time fuses. The delays are activated at the same time as the shells are launched, communicating fire a predetermined time after the shells leave the mortars. Even without such exotica, impressive results can be achieved through accurate choreography. However, if the timing were perfect, there would still be no escape from the laws of physics, namely that light travels faster than sound. Unless each audience member can be equipped with a headset, there is only one specific viewing distance where a choreographed display has maximum appeal – and even then, noises of the fireworks themselves may detract from the intended effect. Thus, while shooting fireworks to music has become increasingly popular, wise operators realize its limitations, and budget their materials accordingly. Instead of striving for precise timing, one important consideration is to choose shells which fit the "mood" of a particular musical composition.[132] Willows tend to harmonize with slow or romantic melodies, big chrysanthemums with dramatic overtures and marches, hummers perhaps with a polka or caprice. Consistency is also important. If, for example, serpent shells are chosen for the initial gallop music in von Suppé's *Light Cavalry Overture*, serpents should be fired again when the same theme reappears later in the piece. Finale barrages and other very noisy segments are usually better without any music at all, although they can be enjoyable if it gradually fades out as the firework sounds take over.

Whether or not music is involved, a little forethought is in order to keep from wasting money on inferior effects. Amateur groups that fire one or two displays a year cannot be expected to know the finer points of each type of shell, or to keep track of the constantly changing quality of different Chinese brands. However, it is amazing how many enthusiastic volunteers do not bother to learn anything at all about the material they are buying. With an attitude that "fireworks are fireworks" and a tendency to order them in the last week of June, it is surprising that the results are not worse than they are. Most package deals are promoted on the basis of shell count, with the predictable result that they rely heavily on the cheapest grades of three- and four-inch Chinese peony effects. Even where there is a good variety of material, it is often spoilt by poor display design – not only by the amateurs but by professional operators with the latest electrical equipment. Salutes, for example, are useful in many ways, but there is no point in shooting them with crossette shells or other subtle effects. Pattern shells such as hearts are usually best in volleys, with several of the same kind together, instead of being scattered amongst other kinds of shells. According to Lancaster[139], "...it is all too easy to end up with a messy 'salad' of colours which allows you to show off nothing to its best effect. Another mortal sin is to have a wonderful Golden Willow Shell completely obscured by brighter low level fireworks." The pace and duration of a display are also important. In some countries, firework exhibitions may last for several hours, allowing elaborate individual pieces to be enjoyed in a leisurely manner. In the United States, where there is a taste for noisy and fast-paced entertainment in general, even the largest displays rarely last much more than half-an-hour. The more material used, the more important it becomes to shoot it in a coordinated way. "Saturation bombing" can be impressive for brief periods, but too many modern displays seem to degenerate into competitions to determine who can fire the most shells in a given amount of time.

Reloading mortars during a display is discouraged by some safety advocates, but it is widely practiced for several good reasons. Relatively few mortars are required, so good steel ones may be used without making the display kit too inconvenient to move around. The plan can be changed at any point; certain types of shells may be scratched from the program if they are not performing well or if a sudden change in weather makes them inadvisable.

Japanese display firing technique differs markedly from what is usual and customary in western countries. All sizes of shells through 12" are typically fired from mortars above the ground, tied to stakes. In the normal, or "slow fire" technique, loose powder is poured into the mortar, the shell lowered onto it, and the whole ignited by dropping a lighted star (called *sindoro*), perhaps containing a small percentage of ferro-titanium for sparks, into the tube. However extraordinary this procedure may sound to a westerner, that the practice still continues is a testimony to the correct performance of the vast majority of the shells. The Japanese also prepare shells especially for "quick shooting"[216] or *haya-uchi*, which do not have leaders, and have their lifting charges enclosed in a minimum of thin paper. The top of each shell (opposite the time fuse and lifting charge) is fitted with a piece of paper tubing, which serves as a handle and also prevents the shell from turning as it slides down the tube. To prepare for firing, a metal coil is heated red hot in a brazier and placed at the bottom of the steel mortar, after which a shell may simply be dropped onto it. The hot metal instantaneously burns through the paper to the lift charge, and the shell is fired. As many as ten shells can be fired in quick succession before the coil cools too much and has to be replaced with a freshly-heated one (Photo 15-43). The method has the advantage of eliminating the handling of loose powder on site, and not requiring the *sindoro* and its striking strip, but there are other drawbacks. The lifting charges of the shells prepared in this manner are vulnerable to handling, and the presence of an open fire to heat the metal coils in close proximity to the fireworks is a safety concern. Neither of these Japanese methods of firing is known to be in use in the United States or other western nations.

Commercial shells vary slightly in size, as do mortars; thus, when preparing for a hand-fired display, it is best to check the fit of any dubious ones in advance. This means any shells that appear lumpy or which have loose baggy lift wrap, and all long multi-breaks. Cylinder shells that fit snugly, but will still slide in a mortar, can be fired, using a stick to push them all the way to the bottom if necessary. However, it would be very dangerous to try to do this in the middle of a display when there could be sparks in the mortar from the previous shot, so any such tight shells should be preloaded. Before the display begins, all shells should be divested of any plastic wrap or extraneous material, and should be inspected for damage such as torn or missing leaders, leaking powder, severe dents, or water damage. Next, they should be carefully sorted by size – one of the most common mishaps in displays fired by "local talent" is that of loading a shell into a mortar one size too large, causing a burst very low if not actually on the ground. Five-inch shells seem to be more subject to this problem than others, partly because they vary so much in type and diameter, and perhaps also because people tend to think in terms of "even" sizes and a five-inch looks very large to someone not accustomed to handling display fireworks. It is not a bad idea to place the main group of five-inch mortars at the opposite end of the line from the sixes. More importantly, shells should be kept in "ready boxes" with only one caliber in each container, and each ready box should be directly behind the mortars of the appropriate size, thirty to fifty feet at least, from the firing line. Wooden boxes with hinged lids can be built for this purpose, but large garbage cans with lids work very well. The main consideration is to open the lids as little as possible and to close them quickly after removing each shell, to protect the remaining shells from sparks or stray garnitures. Unless there is a shortage of crew members, it is best to have a separate loader for each caliber as well. After each volley, it is well to have a different person check the fired mortars, extinguish sparks, and if there is an excessive amount of smouldering paper, clean out the offending mortar before the group is reloaded. A broomstick with a few nails driven through it is the standard tool for this job, although a true cannon worm is even better. In extreme cases, it may be necessary to swab a mortar with a wet rag wound around the cleaning stick. Several buckets of water should be handy for this and other possible emergencies.

Most firework safety falls into the category of common sense, and it is hoped that the reader's intelligence will not be insulted by any of these observations. Even the most experienced shooters can make silly mistakes when hurrying about in the dark. Probably the most important precaution is to avoid placing any part of one's body over a loaded mortar, or one which may be loaded. The smallest shell in common use, the three-inch spherical, is approximately the size of a baseball, and it leaves the mortar with more velocity than the best professional pitcher could give it. Even without exploding, such a projectile can cause broken bones or severe head trauma, including death. Safety glasses or goggles offer protection from flying stars or other shell inserts; long trousers and boots are to be preferred over shorts and sandals for the same reason. The value of more extensive safety gear is arguable. Many crews wear hard hats, but they offer no protection from a shell or mortar fragment coming from below, and would not necessarily save a person in the unlikely event of a heavy shell striking him after a fall of several hundred feet.

In the United States, most hand-fired displays are ignited not with the obsolescent portfire (*q.v.*) but using standard road flares (fusees), which are available with a variety of burning times from five minutes to thirty minutes or more. Their inside diameter of ⅞" is a perfect fit for a piece of broom or mop handle, which can be slid into the open bottom end of the flare and taped into place. A handle makes it easier to ignite a leader without being badly off balance when a quick getaway is required. Some operators like to use a propane or butane torch with a long nozzle. Matches or cigarette lighters should not be used, because they are easily blown out by a breeze, and they place the firer too close to the danger zone.

In the case of the true "dud," where the leader burns but the shell does nothing, crew members should wait a minute or two before approaching the mortar. The mortar then should be marked, and may be covered with a light board to prevent it from being accidentally loaded again, and left until the display is over. Many operators pour water into the mortar before covering it, but this is likely to make the shell swell enough that it will be difficult to remove, and it will take hours or even days of soaking before all the shell contents are completely deactivated. However, where dud shells are to be destroyed by water instead of by burning, it does not hurt to have a head start on the process.

As noted previously, with the exception of salutes, most types of shells can explode in a steel mortar without causing significant damage to it. The upward spray of stars and other garnitures from a premature burst is called a "flower pot;" it usually does no serious harm to anybody as long as the crew members are paying attention and the ready boxes are closed. After such an occurrence, the mortar should be checked with extra care, and if there is any doubt about the strength of the bottom, or if there are plenty of other mortars in the same size, it should be covered until it can be dug up and examined carefully. Incidentally, a sure way to cause a flower pot is to place a shell in the mortar upside down; this is not as uncommon as might be expected and happens mainly with ball shells. Most shells are marked with arrows, but darkness and excitement conspire to make them easy to overlook. Inexperienced shooters who are not told any better may associate the pointed end with the nose of a skyrocket, while a shell which has a large rising tail effect, also covered with paper, may look equally lumpy on both ends. If the hanger loop of a ball shell should break so that the shell hangs almost upside down when held by the leader, conditions are ripe for this embarrassing and potentially dangerous blunder. If the "whoosh" of a leader is followed by a weak "poof" and a large cloud of smoke, it is time to take cover. Large, hard-breaking ball shells are more likely to burst a mortar than other common types of star shells, and there is another hazard associated with them as well. This is the "muzzle burst" in which the shell explodes just as it leaves the mortar. The cause of this phenomenon is poorly understood, but is likely to involve the time fuses, or perhaps ignition from friction of shifting shell contents. During a muzzle burst, the shell appears to perform normally but at a dangerously close distance to the display crew; the explosive force can be enough to burst an eardrum or drive burning stars into the body cavity. Extra care should be taken with chrysanthemum or peony shells in six-inch and larger sizes, particularly those obtained at "bargain" prices.

A bombshell which leaves its mortar and reaches a normal altitude, but does not burst, is sometimes called a "black" shell – but whatever it is called, the danger of leaving such a projectile unrecovered is obvious. Those who load and shoot hand-fired displays are usually too busy to watch the results of their labors, except for a few brief glimpses. The crew chief should be able to watch most of the shells burst, but ideally there will be several observers in different positions to watch carefully for any shell coming down "dark." Teamwork makes it easier to find any unexploded devices, immediately after the display if possible, failing that at first light the following morning. Fortunately, shells rarely explode from impact alone, but those weighing more than a pound or two often crack open on striking hard ground. This makes them less hazardous than they would be if the contents were still confined, and easier for the cleanup crew to destroy, either by soaking or by burning. Salutes or bottom shots, which may be leaking gray or silver powder, should not be burned because large amounts of flash powder can explode with great force even when poorly confined. Other shell components may be burned in a bonfire, preferably built in a pit, if the location permits. Special effort should be made to find and destroy any small explosive inserts, ranging from "M-80" size to two-inch reports, which can be difficult to see on rocky or brushy ground. Such devices need not come from an unexploded shell; more commonly they simply fail to ignite when the rest of a shell's components work properly. Unexploded saettines or timed report units are especially dangerous to curious children, because they are about the same size as many consumer fireworks but are much more powerful. Prompt removal of these and other litter will help preserve the fireworks tradition for the next year.

Chapter 16

Materials Used in Pyrotechnics

It is not possible to cover exhaustively here every variety of charcoal or resinous binder in use. Often, different materials of the same class may be used almost interchangeably. For instance, in Japan, rice starch and hemp charcoal are commonly used, whereas in the United States, dextrin is the most common water-activated binder, and commercially available charcoal is almost exclusively made from hardwood. Some materials, such as boron, are important in military pyrotechnics but are absent in fireworks because they do not produce useful visual effects, quite apart from their cost. On the other hand, the expensive dark "pyro" aluminum plays an important rôle in fireworks, but not in military devices.

Aluminum

Aluminum is the low-cost fuel of choice for many effects depending upon high temperatures and fast reactions. The oxidation products (chiefly alumina) are solid at high temperatures (see Table 16-1) so flame temperatures attainable with aluminum approach those of titanium and zirconium. Aluminum is useful on account of its being stable in mildly acidic media. It is also a necessary material for making many pyrophoric metals, *e.g.*, Raney nickel. But because aluminum does not form transparent gaseous products as does magnesium, pyrotechnic colors utilizing it are often "muddy" or washed out. For this reason high percentages of aluminum are not used in color compositions, although it is used in tremalon and streamer stars. On exposure to air, aluminum normally forms a tightly adhering coating of the hydroxide [$Al(OH)_3$], which may easily be dissolved in alkaline media such as a solution of sodium carbonate. Aluminum powder is stable with oxidizers (chlorates, perchlorates, nitrates) to at least 80° C, and is compatible with ammonium perchlorate. Aluminum exothermically forms intermetallic compounds with nickel, palladium, and platinum[100].

Aluminum powder is manufactured in two forms with distinct differences in performance and subsequent usage: flake (known as "leafed" aluminum, or "leafing" in the pigment industry), and atomized (granular). Flake aluminum is available in different grades (according to particle size) from coarse flakes to "dark pyro." These powders tend to be dirty and unpleasant to work with, less reliable in quality and performance, but are the necessary choice for many applications; German "dark pyro" aluminum is a staple in the firework-maker's inventory. It is not really very common; one source is Gloria Bronze Farbenwerke, D851, Forth/Bay, Germany. It is made from burned paper-backed foil scrap and it contains a little carbon which helps to make it easily ignitable. The size distribution of the flakes greatly affects the quality of the visual effects which can be achieved. For instance, Shimizu[216] reports that to produce "waterfalls" he adds flakes of 5 mm diameter to ordinary 170 μm flaked aluminum.

Atomized aluminum also comes in a wide range of particle sizes. Sieved grades are typically −325 mesh, although coarser grades are common. Purities are high (99+ %) and this aluminum is specified in military ordnance items. Photoflash mixtures often contain atomized aluminum[169] (see Chapter 17). Certain first fires (*e.g.*, CuO/Al) contain aluminum as well. Granular aluminum is the most typical fuel in thermites. Atomized aluminum is clean, cheap, and its quality and particle size are more reliable. However, mixtures containing it are more difficult to initiate than would be the case if a flake aluminum had been used. In military pyrotechnics, it is the most commonly used, and in fireworks, it may often be advantageously used in place of "bright" aluminum, depending on the particular composition.

Ammonium Nitrate

Nitrates are less costly and safer to handle than the respective chlorates and perchlorates, but on reaction, nitrates produce gas making them undesirable for any application in which pressure build-up cannot be tolerated. Ammonium nitrate, in addition, changes in crystal density with increasing temperature* – a property making it undesirable for use in cast propellants. Moreover, it is deliquescent, slow to ignite, and in combination with chlorates it can become dangerous owing to the tendency toward the formation of unstable ammonium chlorate. The capacity of ammonium nitrate to act as an explosive when sensitized with a metallic or carbonaceous additive is well known. Indeed, any impurity may catalyze its explosive decomposition (See Chapter 2, p. 8).

Ammonium Perchlorate

Ammonium perchlorate is one of the principal oxidizers found in composite propellants because, mixed with the appropriate percentage of carbonaceous fuels, the products are completely gaseous. When used with metallic fuels, it forms a white smoke of metal oxide; the hydrolysis of metallic chlorides (water being another reaction product, as well as a constituent of air) also contributes greatly, as in the similar example of HC smokes.

Ammonium perchlorate is not compatible with magnesium. If moisture is present, some of the NH_4ClO_4 dissolves to form ions of NH_4^+, ClO_4^-, H^+, and OH^-. These can combine to form $HClO_4$ and NH_4OH. In the presence of magnesium, $Mg(ClO_4)_2$ can also form. $HClO_4$ will ignite vigorously on contact with

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* The transition NH_4NO_3 (IV) → NH_4NO_3 (III) occurs at 32.23°C.

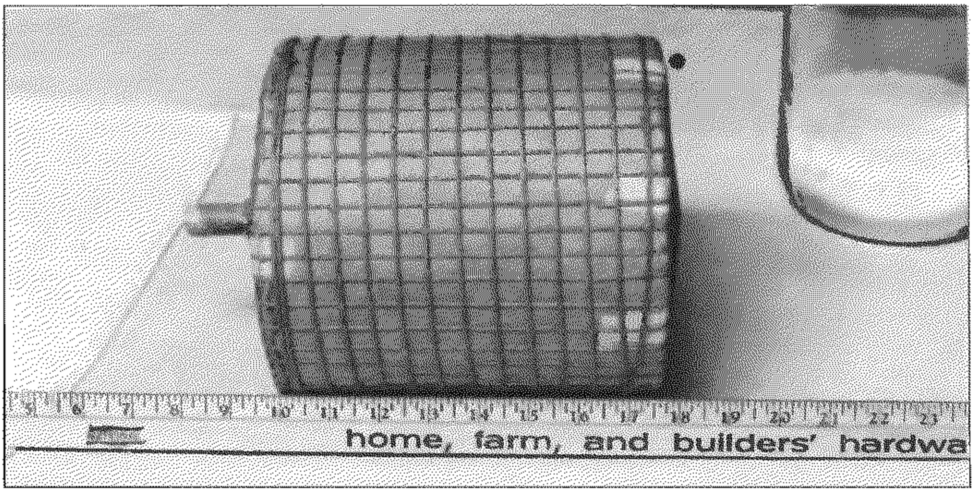


Photo: Barry Bush

Photograph 15-32. 8" shell after spiking.

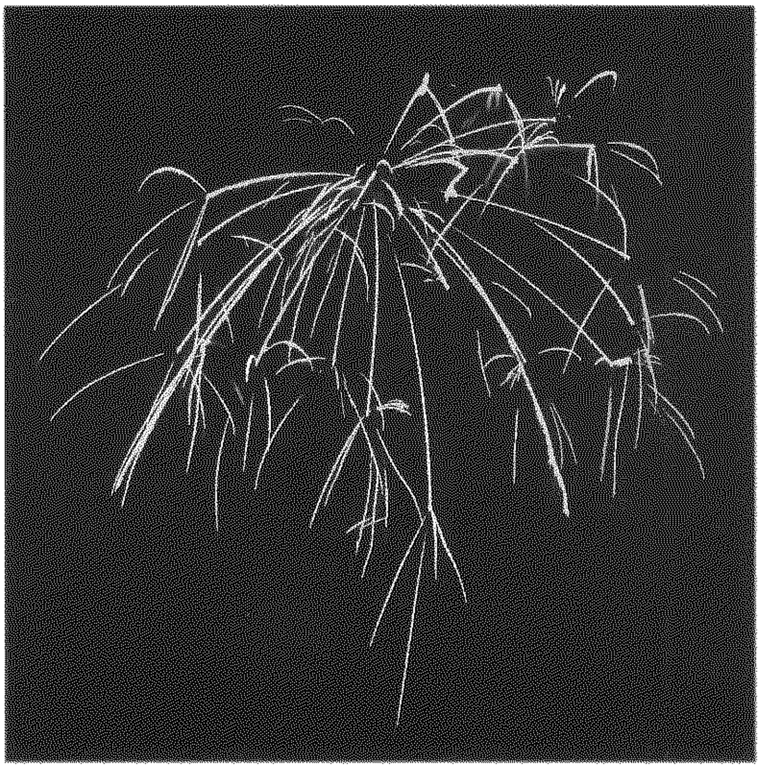


Photo: Ken Clark

Photograph 15-33. Crossette shell. The absence of bright flashes at the break of the crossette comets is an æsthetic advantage of traditional dark report composition.

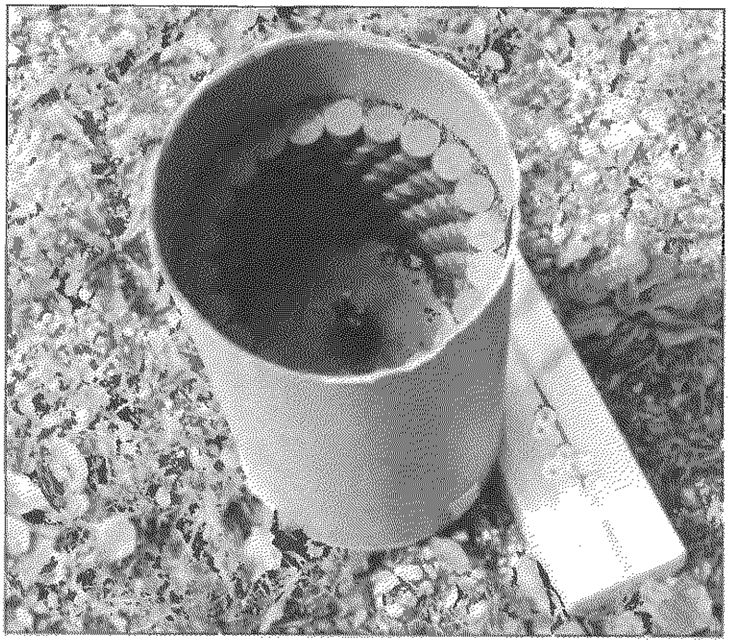


Photo: Barry Bush

Photograph 15-34. Break of pumped stars assembled with final report. These stars still need to be primed in situ, *as described in the text.*

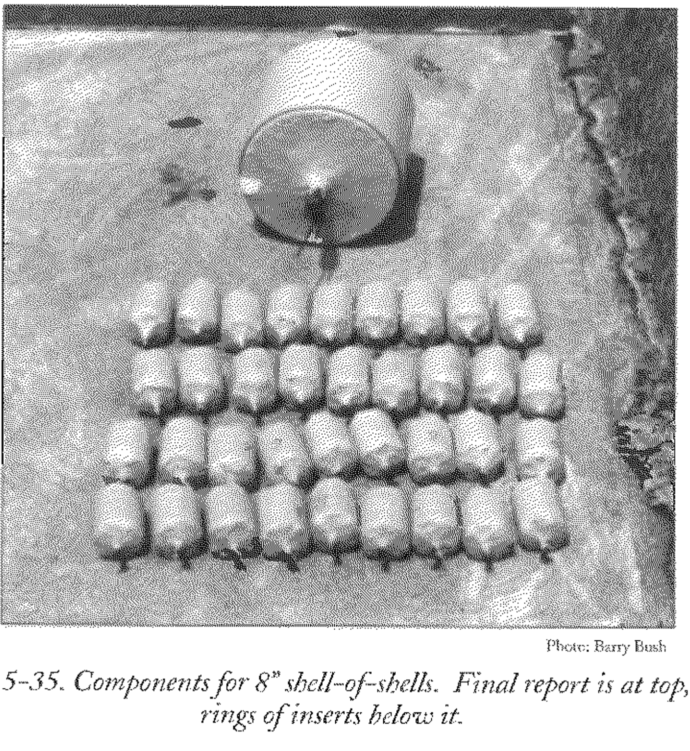


Photo: Barry Bush

Photograph 15-35. Components for 8" shell-of-shells. Final report is at top, four timed rings of inserts below it.

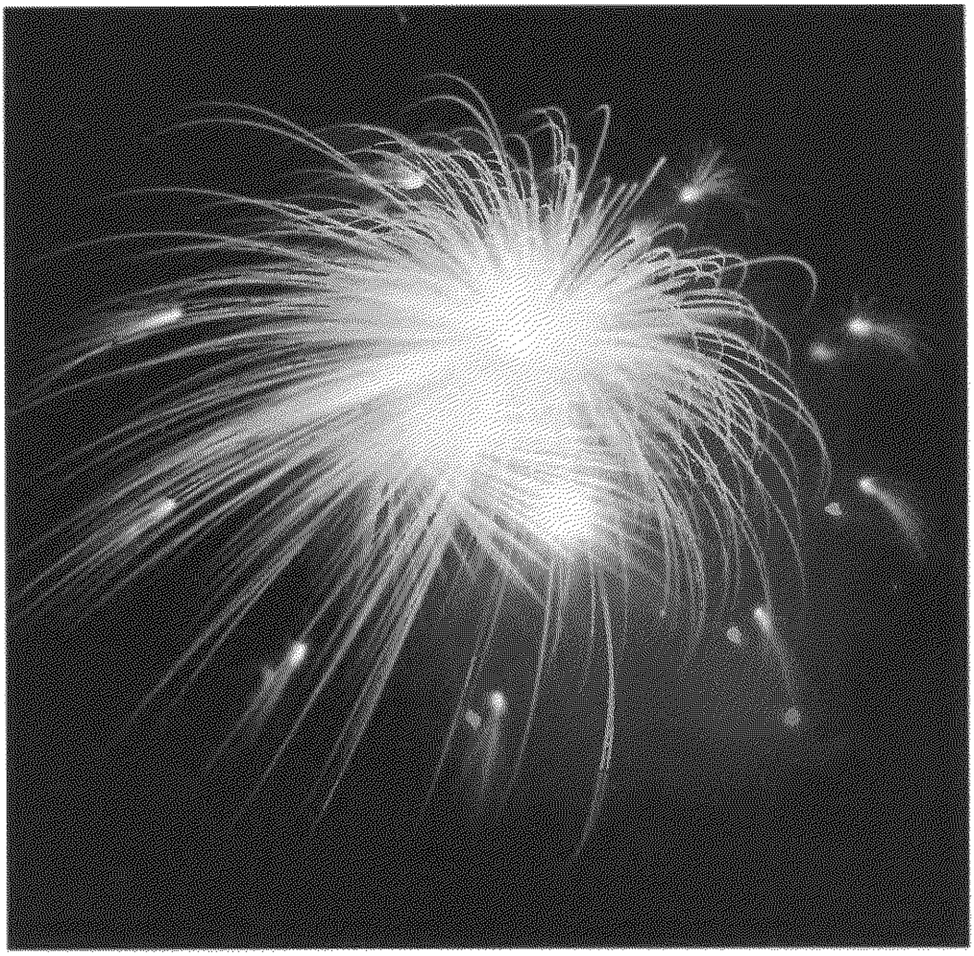


Photo: Mark E. Miner

Photograph 15-36. 8" single-ring shell-of-shells with heavy report.

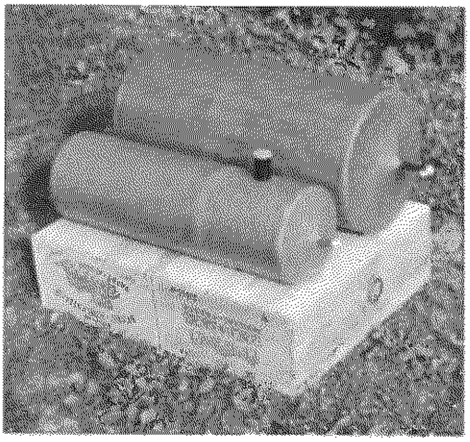


Photo: Barry Bush

Photograph 15-37. 8" and 12" multi-break shells. The 35mm film canister and claret cases show scale.

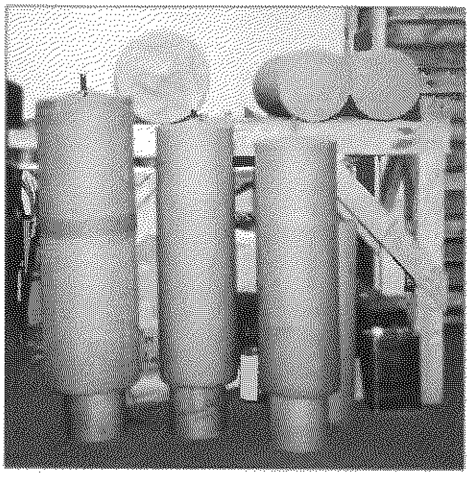


Photo: Michael S. Swisher

Photograph 15-38. 12" and 10" multi-break shells by R. Spychaj and B. Bush in process of completion.

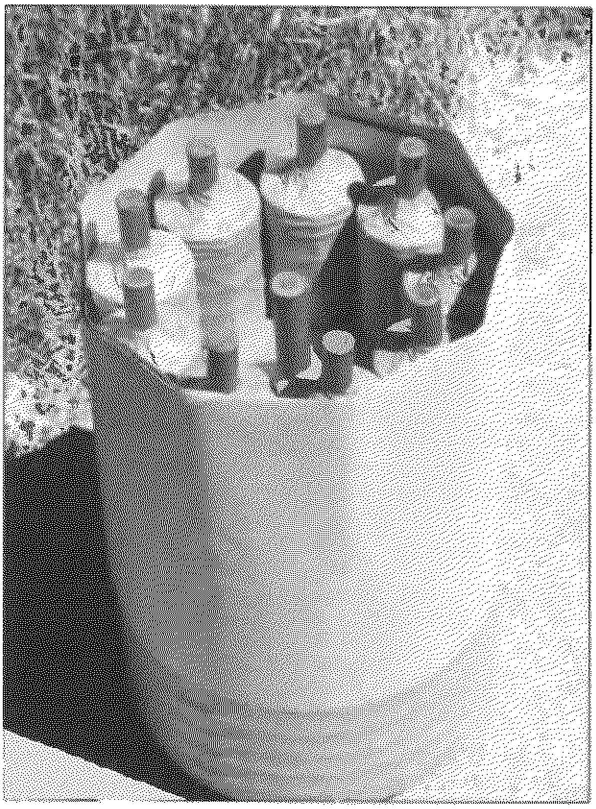
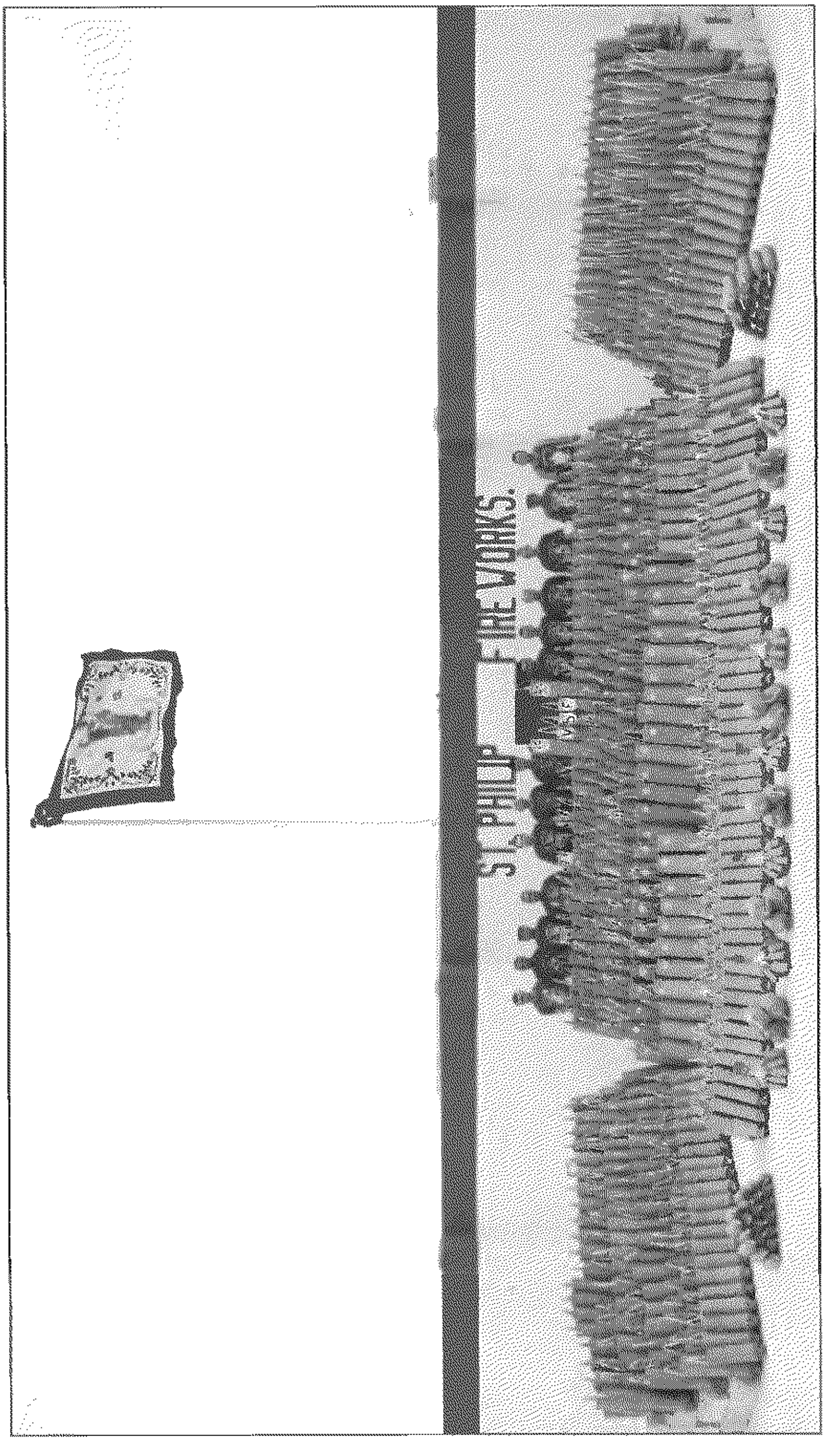


Photo: Barry Bush

Photograph 15-39. Rondelles arranged in ring atop final report. The paper band holding them in position is not used in shell construction; it is used only to show position of the rondelles for purposes of the photograph.

PLATE XXI



Photograph 15–40. Aerial shells for a typical Maltese festa, St. Philip's Fireworks factory, Zebbuġ, Malta.

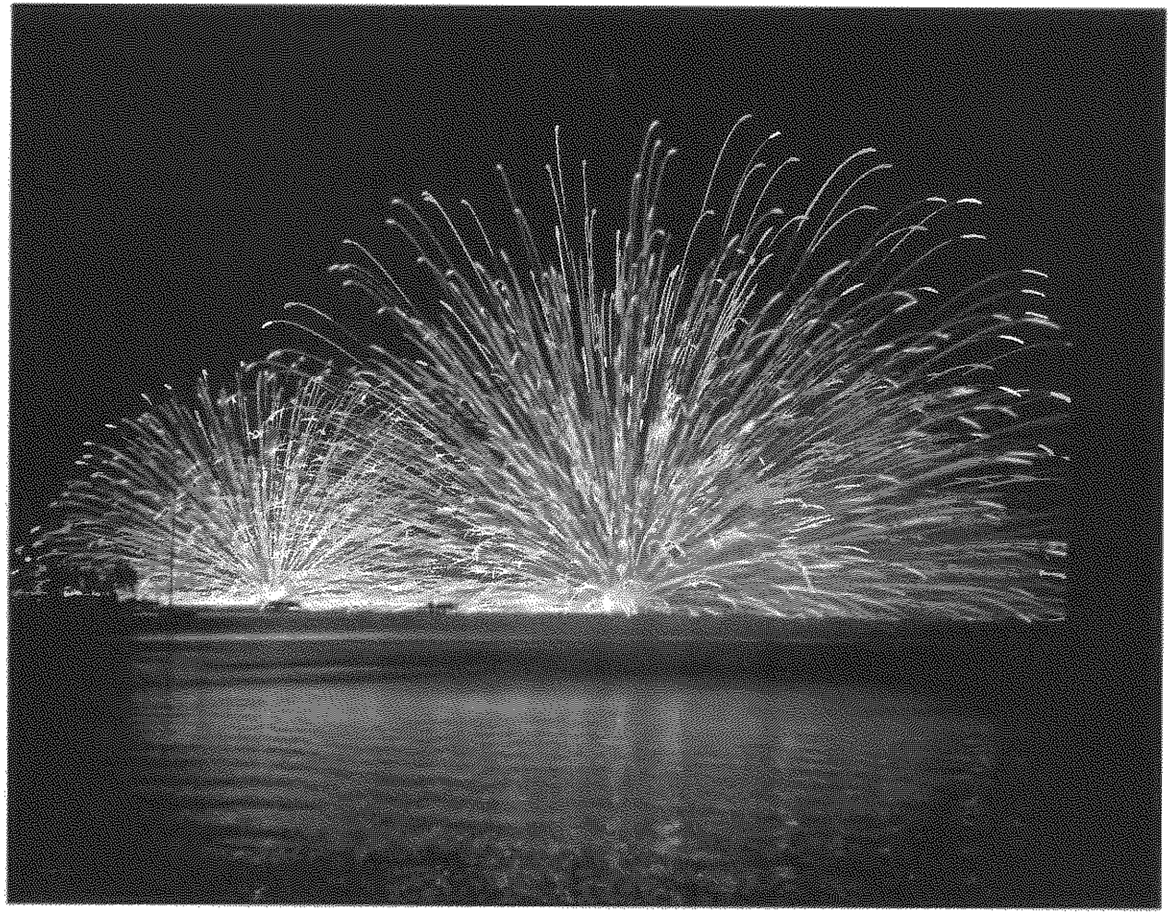


Photo: Kiminari Onozato

Photograph 15-41. Water shells.

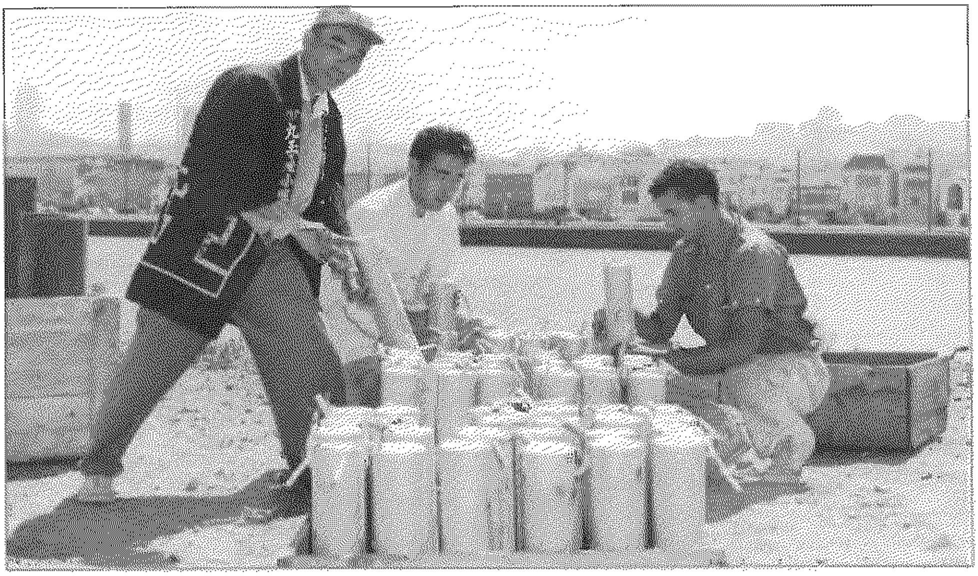


Photo: Jim Wommack

Photograph 15–42.
Pre-loading shells for a display. Mortars are held in boxes filled with sand.

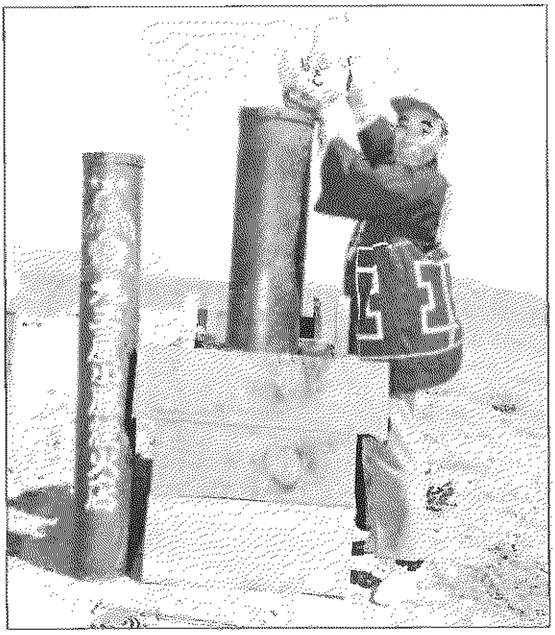


Photo: Jim Wommack

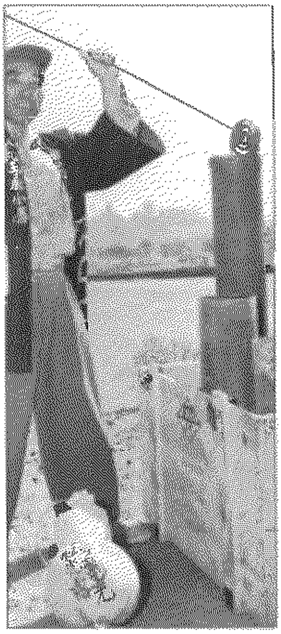


Photo: Jim Wommack

Photograph 15–43. Japanese quick-firing method. Left: metal coil and poker are shown in front of mortar. Right: poker is used to drop the metal coil into a mortar. In actual use, the coil would be red-hot. Demonstrating the technique is Toshio Ogatsu, of Marutamaya Ogatsu Fireworks Co.

U.S. Navy photo by Lieutenant Karl Rauch

Photograph 17-1. An F/A-18C Hornet, *assigned to Strike Fighter Squadron One Four Six (VFA-146), the "Blue Diamonds," deploys flares during a Competitive Training Exercise (COMPTUEX), the Pacific Ocean, Aug. 16, 1999.VFA-146 is assigned to* USS John C. Stennis *(CVN 74).*

organics and detonates by shock and heat. $Mg(ClO_4)_2$ is also a fire and explosion risk in contact with organic materials.

Ammonium perchlorate's corrosive effect on magnesium can be suppressed by suitable surface coating, as discussed below under the heading magnesium. The avoidance of ammonium perchlorate in systems which also contain potassium chlorate is stressed, as in the similar case of ammonium nitrate.

Ammonium perchlorate is not hygroscopic, but care must be taken to avoid exchange reactions with certain metal ions, the perchlorates of which are hygroscopic. Encapsulating either the oxidizer or the fuel in a binder will greatly aid in maintaining the stability of the formulation.

Shimizu[217] reports that ammonium perchlorate-based fireworks stars produce particularly clear colors, but that such stars have limited storage life when primed with black powder because of the formation of deliquescent ammonium nitrate.

Antimony and Arsenic Sulfides

Mixtures of antimony trisulfide, Sb_2S_3,* with many common oxidizers are sensitive to shock and friction. For this reason, such mixtures are important in stab primers in which they take the place of more hazardous primary explosives. Antimony sulfide is obtained by liquation of the naturally occurring mineral stibnite and subsequent pulverization. The material thus obtained is a relatively pure, dark grey powder, showing crystalline luster if the particle size is not too small. It is to this appearance that the old German name for the substance, *spießglanz*, alludes. Shimizu[216] reports that whereas mixtures of antimony sulfide with potassium chlorate are sensitive both to shock and to friction, mixtures with potassium perchlorate are sensitive to friction but not to shock. Antimony sulfide mixed with ammonium perchlorate is sensitive to shock but not to friction. Mixtures with potassium nitrate are insensitive to both. The orange pentasulfide, Sb_2S_5, is not a common pyrotechnic ingredient.

Historically, realgar, As_2S_2, has been used in report (sound) compositions in combination with potassium chlorate. In combination with potassium nitrate, it is useful in white stars, smoke compositions, and other effects. Concerns about its toxicity (it forms arsenic trioxide on combustion and may contain it as an impurity) have made it a rather unpopular ingredient. Realgar is at present also much more expensive than antimony sulfide. Orpiment, As_2S_3, was historically preferred for the "flower pot" fountain effect in fireworks (see Chapter 15).

Alkaline Earth Chromates

Apart from the carcinogenicity of hexavalent chromium, the alkaline earth chromates possess a number of desirable properties for pyrotechnic applications. When reacting with fuels, such as boron or zirconium, they do so in an essentially gasless manner. Such mixtures, by adjustment of their proportions, can be made to deliver an exact amount of heat and they are therefore useful as heat powders for activating molten electrolytes, and for military and civilian self-heating cans of food, etc. The suitability of these combinations stems from the aforementioned low gas evolution, the formation of a firmly sintered residue, great ease of ignition, and relatively gentle reaction.

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* By convention this compound is understood when "antimony sulfide" is used without the "tri" prefix.

The static sensitivity of boron/chromate mixtures is greater than that of similar mixtures containing metallic fuels. A mixture containing 88% iron, 12% potassium perchlorate with a barium chromate/zirconium igniter is used in a static-insensitive heat device with an energy output of 400 cal/g and a gas evolution of 0.1 ml/g.

Ellern[70] reports that the range of heat output of barium chromate mixtures can be significantly extended by substitution of strontium or calcium chromate because of their lower molecular weights. Alkaline earth chromates are anhydrous, are not hygroscopic, and do not form hydrates even when slurried with water. Highly calorific mixtures with calcium chromate are excellent fire transfer compositions and are used in squibs and as gasless heat powders in general.

Barium Compounds

Barium nitrate is stable and non-hygroscopic, and is a useful oxidizer in many pyrotechnic mixtures, including some priming compositions (see Chapter 12). It is also a coloring agent, producing green light when used with a chlorine donor such as polyvinyl chloride (PVC). Without the chlorine donor, and using aluminum or magnesium as the fuel, the light produced is a brilliant white. Lancaster[139] gives a report composition containing 68% barium nitrate, 23% pyro-aluminum and 9% sulfur, which is less shock-sensitive than the more common perchlorate flash report mixtures but the barium nitrate flash compositions lack the sheer power and ease of ignition of the perchlorate type. Barium nitrate is a relatively inexpensive material, costing, at the time of this writing, less than one dollar per pound when purchased in bulk quantities. Disadvantages include toxicity and a relatively low oxygen yield.

Barium chlorate can produce deep green colors without the use of additional chlorine donors. Its use was first endorsed in 1836 by Chertier[32a]. Today it is still used in display fireworks, but is rarely seen in military pyrotechny. Barium chlorate is believed to be more sensitive to decomposition by exposure to sunlight than is potassium chlorate, and mixtures containing it are sensitive to shock and friction. It is also considerably more expensive. *Barium perchlorate* has similar pyrotechnic properties, but is far too hygroscopic to be useful in commercial items.

Barium carbonate, in most mixtures, gives very weak flame coloration. Those interested in fireworks may recall the mixture quoted by Brock[26] of $Ba(ClO_3)_2$, 9; $BaCO_3$, 5; and Al,10. Inclusion of 21% $BaCO_3$ (probably as a diluent and phlegmatizer) does not prevent this composition from giving a surprisingly good color.

Black Powder and Related Materials

After many centuries as the all-purpose propellant and igniter, black powder is even now of great technical importance. While modern ignition mixtures have replaced black powder in most military applications, it still holds its own as the igniter for large caliber gun propellants. In this application it has the desirable qualities of being an effective flash reducer and of being a better igniter for large-grain smokeless gun propellants than are other smokeless powders. Another property is its ability to ignite at low pressures; for this reason, black powder was at one time used in anti-aircraft rounds as a fuze composition. The rôles of sulfur, moisture, and volatiles in the charcoal are complex and were made the subject of a recent review article[201].

Many attempts have been made at finding a substitute for black powder and the effort is a continuing one[258]. The typical thrust of research into black powder substitutes is directed at replacing the potassium nitrate with perchlorate and reducing the variable properties of the charcoal by replacement with alternate fuels such as solid aromatic compounds. One patented[184] substitute for black powder is Pyrodex®. It has the virtue of being possible to manufacture with less specialized facilities than those required for black powder. The performance of Pyrodex was compared with that of black powder in a recent study[47]. It appears that residual moisture phlegmatizes the composition sufficiently to permit the use of perchlorates, which otherwise would generate high pressure spikes rendering the powder unacceptable as a propellant. Pyrodex was believed to function as well as black powder but to be safer to handle. The impossibility of a "safe" powder was tragically demonstrated when the inventor and his associates were killed in an explosion which destroyed the plant. Pyrodex continues to be made as a replacement for black powder in firearms and munitions and is marketed by the Hodgdon Powder Company of Shawnee Mission, Kansas.

Another, reportedly comparable, substitute appeared under the name "Golden Powder," consisting of 60% KNO_3, 35.8% ascorbic acid and 4.2% sodium erythorbate. The manufacturer claimed a water-soluble residue and, because of the absence of sulfur, less barrel corrosion. Golden Powder is apparently off the market; more recent variations include Black Canyon, Black Mag, and Clean Shot. All of these substitutes find application mainly as propellants in muzzle-loaders.* Some have been investigated for military and fireworks applications, but compared with black powder, they appear not to be cost-effective. It is also worth noting that a material which can replace black powder in one application is not necessarily useful in another. For example, pellets of a potassium nitrate/boron composition may be regarded as a "black powder substitute" in certain rocket igniters. However, such a mixture is by no means suitable for use as a propellant in black powder firearms!

Black powder doubles as igniter and propellant in military flare ejection systems and in some signal rockets. More significantly, however, black powder has held its own in fireworks, as igniter and propellant, and in delay fuses for aerial display shells, as discussed more fully in Chapter 15. As with large caliber gun propellant ignition, black powder has resisted the influx of competitors because of its relative cheapness and because of its singular effectiveness. While no precise data on black powder consumption for this purpose are available, it must rival the quantities procured for military use, more than a thousand metric tons annually[254].

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* Undoubtedly, one of the reasons Pyrodex gained wide acceptance among shooters was that its creators managed to have this propellant classified in the same group as smokeless powders under shipping and storage regulations. Black powder cannot be sent by post, and until recently, the major private delivery service in the United States refused to handle it as well.

Except for use in a few specialized fireworks items (which are rarely seen), black powder is not made by the fireworks makers themselves. The procurement of black powder has become a matter of ever-increasing difficulty. Since outside of the fireworks industry, smokeless powder has almost completely replaced black powder, steadily decreasing demand has led to a corresponding decrease in production and there is only one non-military supplier surviving on the North American continent. An interesting aspect of this production history is that the number of suppliers suffered attrition not only for economic reasons but because of a poor safety record which is, in part, a reflection of the risk in the manufacture and handling of black powder. The most famous producer has been the Du Pont Company, but in 1973 it sold its last surviving plant in Moosic, Pennsylvania to GOEX, Inc., which in turn has suffered two serious explosions since, and has now relocated in Louisiana.

There still remains, however, a need for black powder for military use, and the U.S. Army has constructed a new facility at Charlestown, Indiana. This plant uses a new jet mill process,[226] also known as the Løvold process[153] which is semi-

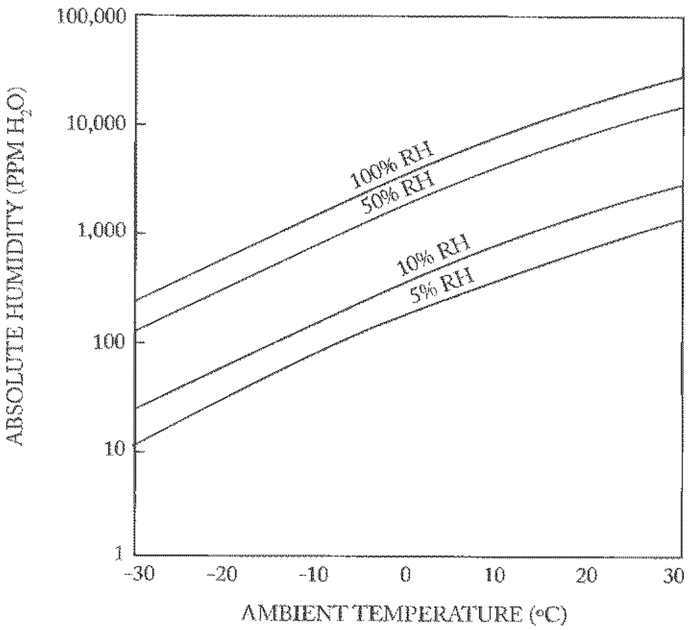

Figure 16-1. Moisture content of air as a function of temperature.

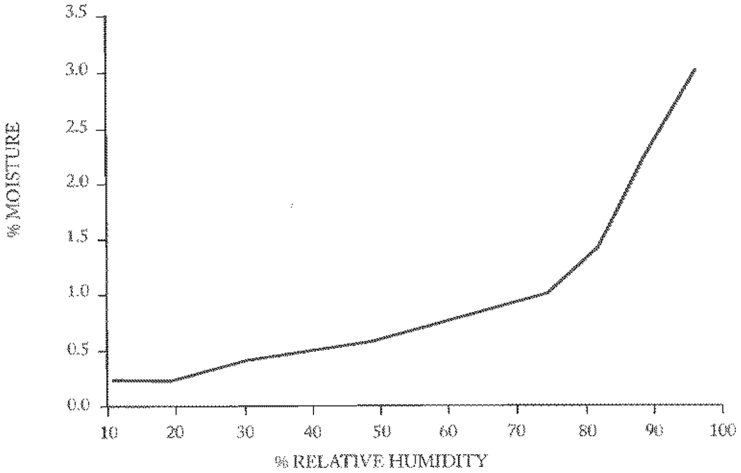

Figure 16-2. Black powder moisture content vs. *relative humidity*[162].

continuous and automated, and for which an improved measure of safety is claimed. Nevertheless, Dyno Industrier, A/S, a Norwegian manufacturer using the jet mill process, has also suffered a major explosion with loss of life. The accident occurred on a day when the outside temperature was −22° C. The process was investigated by Løvold and Middleton[154] who measured the spark initiation sensitivity for black powder dust to be 45 mJ. Another investigator, Maki of Kemira, OY, Finland, found the minimum ignition energy of resting black powder to be as low as 6 mJ, or below the minimum static charge energy which can be supported by the human body (60-80 mJ). These findings suggest that unexplained explosions in black powder mills may well be due to static electric discharges. This matter has been considered previously by Løvold[153] and by Stephanoff[226] who specified that the relative humidity within the production facility was to be maintained at 70% and 85%-95% respectively. An absolute humidity of 10,000 ppm would go a long way to eliminate the static build-up which could have been the cause of the Norwegian accident. Fig. 16.1 is a plot of the moisture content of air as a function of temperature. It may be seen that air at 100% RH at −20° C corresponds to only 5% RH at +20° C. Ironically, many ordnance plants and test facilities are located in geographical areas having just such extremes in humidity. Fig. 16.2 shows the amount of moisture in black powder as a function of relative humidity, thereby illustrating the reason for the need to handle black powder at high relative humidities.

Boron and Silicon

Boron surpasses every element except hydrogen and beryllium in heat output on combustion, and is thus an important fuel for military use. Because it is nonmetallic, mixtures of boron with oxidizers have low thermal conductivity, and hence are easily ignited. Although the combustion product, boric oxide, has a low melting point and a high boiling point, in fuel-rich mixtures at temperatures above 1000° C it exists in the vapor phase as boron suboxide, BO. Therefore, it is quite incorrect to describe pyrotechnic compositions with boron (*e.g.*, boron/barium chromate delay compositions) as having gasless reactions; the flame front is propagated by the flow of the gaseous suboxide. Moreover, the common boron of commerce has trace impurities of oxygen and magnesium, among others. Certain grades (*e.g.*, vapor deposited material from the pyrolysis of boranes, or electrolytically produced material) are free of these contaminants. These forms of boron are not nearly as reactive. One such high purity grade is marketed by the Callery Chemical Company. High purity boron, even though quite costly, should be considered when sub-micron particle sizes or reproducibility in composition is important. We must look to the volatility of its contaminants in explaining its reactivity as we do in explaining the higher reactivity of charcoal compared with that of graphite, or of sublimed sulfur compared with that of crystalline sulfur. Even though boron shares its position in the third group of the periodic table with aluminum, it differs significantly in its pyrotechnic properties due to the lower melting point and higher volatility of the oxide.

Like boron, silicon conveys low thermal conductivity and therefore, ease of ignition to pyrotechnic compositions. Silicon is found in many igniter and delay compositions. Calcium silicide is also occasionally used. Pyrophoric silanes (silicon hydrides) have been discussed in a previous chapter.

Carbon, Carbonaceous Fuels and Binders

One of the causes of the variability in the reactivity of carbonaceous pyrochemical mixtures is the many forms of carbon and its compounds which may be used as fuels. This is true whether the carbon is lampblack or charcoal. Graphite is rarely considered because it does not sustain combustion and its lubricating qualities tend to reduce reactivity. Carbon black, also known as acetylene black, has a graphitic structure, and like graphite, is quite non-reactive. Charcoal is the fuel in black powder (and in some black powder substitutes), and when it is present in excess of the available oxygen in a composition, it is ejected from the flame as glowing particles – a much-used firework effect. Charcoal usually contains between 20% and 40% volatile hydrocarbons. Also, charcoal mixtures have low thermal conductance. These two factors make charcoal compositions highly ignition-sensitive.

The porous structure of charcoal allows other molecules (in the case of black powder, KNO_3 and S) to be incorporated by milling or stamping. The mechanism of the incorporation is somewhat controversial; the burning rate of the Løvold type powder is the same or somewhat lower than the GOEX reference standard (see the preceding section on black powder). Considering that the jet mill produces a finer particle size than does the conventional milling process, one would expect equally rapid or faster combustion. It has been claimed that the milling or stamping causes both sulfur and potassium nitrate to be forced into the porous structure of the charcoal, but electron micrographs do not support the idea. R.A. Sassé[204] has speculated that the cause for this discrepancy is that ingredients to be milled are dampened with about four percent water which is absorbed on the surface of the charcoal particles. This model suggests that the four percent bulk water would make the charcoal hold 25% liquid saturated with potassium nitrate.

The systematic study of the pyrochemical properties of charcoal using the methods of instrumental analysis is of relatively recent date[107]. The role which the parent hardwood plays in determining the characteristics of charcoal has been known empirically for centuries[95]:

> Alder buckthorn* is used in gunpowder for evenly burning fuses while alder is used where precise burning is not required. Alder buckthorn charcoal was found to have the lowest spontaneous ignition temperature and the highest porosity (as measured by mercury porosimetry) of the three charcoals and could be the most suitable charcoal for gunpowder because of the ease of ignition.

Charcoal is not pure carbon, but rather represents an undefined intermediary state between its organic origin and the element carbon, retaining both hydrogen and oxygen. Because of this composition and its high absorption capability, it may contain as much as 6% water; black powder specifications allow, therefore, a maximum of 0.70% moisture. The equilibrium water content varies with the relative humidity of the ambient air. At 90% RH, a weight gain approaching 2% may be measured, but at normal RH (20-60%), the equilibrium water content has been given as 0.2-0.6% and between 80 and 90% RH as 1.0-1.5%. This moisture problem can cause the deterioration of the powder and sometimes of its container under unfavorable conditions. Replacement of charcoal by a purer, non-cellular carbon made from sucrose (sugar) is the subject of a U.S. patent (U.S. 2,415,848, 1947). Powders made with such carbon sources are slower burning than regular black powders.

Charcoal is made by pyrolysis of vegetable matter in iron retorts. Its procurement specification should always state the content of volatile matter[200]. The question of controlling the volatile content has been made the subject of a number of recent studies. The problem arises from the fact that the destructive distillation process is not automated, but is performed with continuing monitoring by skilled operators; the optimum volatile content is encountered during the period of maximum decomposition rate[204].

Carbonaceous fuels often double as binders. Shellac was long the standard fuel for chlorate color compositions, sometimes doubling as a binder (it is soluble in alcohol and turpentine). It has mostly been replaced by accroides resin (red gum), which is cheaper, although more troublesome as a binder. Rosin and accroides resin also have better combustion properties with potassium perchlorate than does shellac. Water-soluble binders (dextrins, gum arabic, casein and animal hide glue) have been discussed as essential ingredients of matches.

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* *Rhamnus frangula* Linn.

The binder formerly most often specified for large military flare candles belongs to the class of unsaturated polyesters with added styrene. It is best known by the trade name of Laminac 4116 and is made by the American Cyanamid Company. Since the liquid resin is relatively low in viscosity, it offers the advantage that it may be added to the solid powder without any volatile solvent. The curing agent is 1-2% of methyl ethyl ketone peroxide in dimethyl phthalate (trade name Lupersol DDM) which converts the resin first into a gel state, and then by a strongly exothermic reaction into a hard solid. The reaction is accelerated by cobalt naphthenate. It is inhibited by air so that curing in thin layers may leave a tacky mass. Laminac is usually admixed as 4-9% of the formula weight, and some shrinkage is observed on curing. Notwithstanding its low viscosity, the incorporation with the metallic fuel can be somewhat difficult. The addition of a wetting agent such as polyoxy alkylene polyol (trade name Pluronic F-68) has been recommended. It is also possible to add more styrene as a diluent and this copolymerizing plastic monomer then becomes part of the solid resin. The practice has been to add some acetone or trichloroethylene whenever it appears desirable to facilitate distribution of the resin and to assure complete wetting of the metal powder. Ellern reports heats of polymerization of 130 cal/g of the monomer from which the temperature rise in the copolymerization mass can be estimated[70].

The binder system currently favored is epoxy based and will be explored in Chapter 17. An example is Epon 828, diluted with allyl glycidyl ether (AGE) which reduces the viscosity and about 8% diethylene-triamine (DETA) which is added as a cold curing agent.

The plastic binders that are used in monomer or low molecular weight polymer form, and cured by additives, must be distinguished from fully polymerized synthetic resins, or from natural solid resins which require a solvent (*e.g.*, shellac). The exceptions are materials that flow under pressure. Gilsonite, a natural, pure asphalt, can be stored in a finely powdered state and is easily incorporated in a mixture, but will display good binding power on pelletizing. It tends to leave a gummy residue on molds and rams.

Although they persist in fireworks compositions, the tendency in military practice has been to avoid natural products. An exception is "limed rosin" or calcium resinate which is found in such mixtures as tracer formulations. Of the synthetic resins that are found in pyrotechnic formulæ, polyvinyl acetate and polyvinyl chloride (the latter also a chlorine donor) deserve mention. Polyacrylic resins such as Hycar in methyl ethyl ketone have been used as well[70].

Shidlovskii[214] describes the use of Iditol, a lacquer-type condensate of phenol-formaldehyde. The Germans are said to have used Bakelite A in World War II in tracer munitions. No doubt, there are many more types of synthetic polymeric materials which are potential candidates, but few new compounds have made an appearance, probably because the need to abandon the established materials has not been sufficiently strong. The qualification of a new formulation is a lengthy

Table 16-1. Melting Points and Boiling Points of Oxides

Oxide	m.p., °K	b.p., °K
ThO_2	3470	4670
MgO	3105	(s)
HfO_2	3060	
ZrO_2	2970	4500
CeO_2	2870	
CaO	3200	3800
BeO	2780	
SrO	2690	3270
Cr_2O_3	2603	3280
BaO	2286	3360
Al_2O_3	2327	≈3000
TiO_2	2143	3279 (d)
B_2O_3	723	2338

(s) = sublimes, (d) = decomposes

and costly matter, one which it is preferable to avoid.

Substances that keep powdered materials in free-flowing condition – anticaking agents – may be added to oxidizers used in pyrotechnics, especially potassium chlorate and potassium nitrate. For example, 3% magnesium carbonate is very effective in preventing agglomerations of these materials. Ground sulfur can be kept in a free flowing condition with as little as 0.04% of fumed silica such as Cab-O-Sil®*. Zirconium salts have been recommended as anticaking ingredients for nitrates[116].

Magnesium

Magnesium is one of the most important fuels in pyrotechnic mixtures because it burns at high temperatures, assuring the vaporization and subsequent excitation of emitting species generated from coloring additives. It is especially valued because it can produce colored flames with nitrates. The combustion mechanism of magnesium differs from that of other metallic fuels in that magnesium has a high vapor pressure (see Table 16-2) and a low melting point (923 K), and therefore is easily ignited. Once ignited, it burns in the vapor phase so that the rate of combustion does not depend on the rate of diffusion of oxygen to the metallic surface as is the case, for instance, with titanium and aluminum. Consequently, the rate of combustion is not as dependent on the particle size.† Moreover, the oxide does not dissociate except at very high temperatures (see Table 16-1), so that all of the heat of combustion goes into heating the solid and very little goes into dissociating the reaction product. Consequently, magnesium burns with a

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* Cabot Corp., Cab-O-Sil Division, 700 E. U.S. Hwy. 36, Tuscola, IL 61953.

† This is the reason that Mg is rarely useful as a spark-producing fuel – a rôle well played by Ti and Al.

Table 16-2. Vapor Pressures of Selected Elements[98] in Atmospheres

Temperature, °K	Boron	Aluminum	Titanium	Magnesium
300	4.3×10^{-93}	2.6×10^{-51}	3.1×10^{-75}	5.3×10^{-20}
500	1.2×10^{-52}	4.9×10^{-28}	5.2×10^{-42}	5.3×10^{-10}
1000	9.2×10^{-23}	5.3×10^{-11}	1.4×10^{-17}	1.6×10^{-2}
1300		3.0×10^{-7}	5.2×10^{-12}	0.581
2000	6.7×10^{-8}	6.1×10^{-3}	1.2×10^{-5}	
2500		0.255		
2600	1.4×10^{-4}		5.0×10^{-3}	

hot, luminous flame. With the addition of chlorine, the oxide forms the gaseous chloride which tends to make the flame transparent, making the bright colored effects - the candle power of which is dependent on magnesium – possible.

Whereas aluminum is sensitive to alkaline media, magnesium is strongly attacked by acids. If hygroscopic ingredients are present together with magnesium, it may be attacked by moisture. Magnesium is compatible with the nitrates of potassium, sodium, barium and strontium, and with potassium dichromate. Sodium bicarbonate and oxalate are corrosive, as is sulfur. The use of ammonium salts with magnesium is dangerous, and they must be protected by surface coating, as mentioned above. The presence of any moisture will initiate the redox reaction:

$$Mg_s + 2NH_4{}^{+}{}_{(aq)} \rightarrow Mg^{2+}{}_{(aq)} + 2NH_{3(g)} + H_{2(g)}$$

Protective coatings effective in mixtures containing no ammonium salts include linseed oil, paraffin, and polyester resins. The standard treatment for magnesium to be used with ammonium salts is coating with potassium dichromate[217]. The toxicity and carcinogenicity of the dichromate ion should be borne in mind. Alenfelt[2] has recommended an alternative surface treatment using ammonium metamolybdate and ammonium dihydrogen phosphate.

Magnalium

Magnalium is the name for alloys of the two metals, magnesium and aluminum. Such alloys are brittle and can be easily pulverized. The material most readily available to the pyrotechnist is a 50:50 alloy, with a melting point of 730 K. It is more stable when mixed with oxidizers than is magnesium itself, but its relative hardness can present friction problems.

Magnalium tends to burn smoothly with potassium chlorate and perchlorate, with which compounds it may be used to produce excellent color effects, the compositions having a stability that would not be a property of an equivalent magnesium composition. Magnalium's higher resistance to corrosion allows it to be added as a small percentage to a blue composition, producing the "magnesium blue" which eluded firework makers for so long.

When used with barium or strontium nitrate, or ammonium perchlorate, the mixtures can be adjusted to burn "vibrationally," a reaction harnessed by pyrotechnists in the now-ubiquitous *strobe effect*. It is also the key ingredient to the *crackling effect*, typically in combination with red lead and copper (II) oxide (see Chapter 15).

Phosphorus

Of the four allotropic forms of phosphorus, white (or yellow), red, black, and violet, only the red is of value in modern pyrotechnics. Thermodynamically it is stable above 300° C and when heated below that temperature, it tends to revert to the yellow form. When pure it has no odor but when it is contaminated with yellow phosphorus, it acquires a characteristic garlicky smell. Shimizu[216] reports that the safest process for purifying it is to wash it with hot water. When stored in large quantities the trace contamination will be oxidized in air, causing it to self-heat, possibly escalating to auto-ignition. It is used as an active ingredient with potassium chlorate in toy caps and in matches. Furthermore, red phosphorus is the principal smoke generating agent in all Navy marine location markers,[60] Army smoke grenades and some other smoke generating devices. Much effort has been devoted to the reclamation of phosphorus from production scrap[90]. The references regarding the toxicity of red phosphorus are contradictory. It appears that red phosphorus, when pure, is not toxic, but that when contaminated with yellow phosphorus, it can be deadly. In any event, ingestion is ill-advised. Some of these precautionary remarks really seem quite silly, but one cannot ever be quite sure that the label "non-toxic" would not be taken to mean "edible."

Potassium Chlorate

Potassium chlorate is now made by the electrolysis of potassium chloride with a graphite anode and a steel cathode. Alternately, chlorine can be made to react with slaked lime, yielding $Ca(ClO_3)_2$, which is then reacted with potassium chloride. Potassium chlorate is only slightly soluble in cold water and only moderately soluble in hot water. It is not hygroscopic. Potassium chlorate powder, made by crushing the crystals, tends to cake much like potassium nitrate, but can be made free-flowing by the addition of anti-caking agents. Potassium chlorate is slightly shock-sensitive, even when pure.

One important function of potassium chlorate in pyrotechnic compositions is to generate a high-temperature flame, the chlorine content of which is effective in deepening the flame color by the formation of biatomic ions of the alkaline earth halides, as discussed more fully in Chapter 6. Furthermore, because chlorate requires very little heat* to initiate its decomposition, and does

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* The *in vitro* decomposition of potassium chlorate should be well known to any chemistry student, and proceeds into two stages, the first being a disproportionation reaction:

$$2KClO_{3(s)} \rightarrow KClO_{4(s)} + KCl_{(s)} + O_{2(g)} \quad T>268\ ^{\circ}C\ \text{(Merck)}$$

$$KClO_{4(s)} \rightarrow KCl_{(s)} + 2O_{2(g)} \quad T>400\ ^{\circ}C\ \text{(Merck)}$$

Catalysts, such as MnO_2, allow the complete decomposition of chlorate to chloride and oxygen to be accomplished as a smooth, continuous reaction.

so at a comparatively low temperature, its employment assures ease of ignition, making it useful in stars and other fireworks.

Potassium chlorate-fuel mixtures tend to be sensitive to shock and friction, particularly if the mix contains red phosphorus, sulfur, realgar or antimony sulfide. This property is exploited in stab primer and percussion primer compositions. These are discussed more fully in Chapter 12. The remarkable feat of safely combining potassium chlorate and red phosphorus in the safety match is described in Chapter 11. "Amorces," or toy caps, contain small dabs of potassium chlorate and red phosphorus which are applied when moist. In contact with concentrated sulfuric acid, a potassium chlorate and fuel mixture will ignite spontaneously. Other strong acids may produce the same effect, with varying degrees of delay. It is wise, when mixing large quantities of a chlorate composition, to add a small percentage of a basic salt (*e.g.*, barium carbonate) as an acid neutralizer. Regardless of whether chlorate and sulfur (or phosphorus) mixtures are phlegmatized, they remain prohibited in the United Kingdom[228] for fireworks applications, because the care taken in the assembly of the devices cannot be effectively monitored by the authorities. Rev'd. Lancaster[139] discourages the use of asphaltum or pitch as a fuel or binder in mixtures containing potassium chlorate on account of the possible sulfur content in the asphaltum.

The decomposition of potassium chlorate is catalyzed by heavy metal oxides:

$$2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2$$

The effect is one of lowering the temperature at which oxygen first appears and also of eliminating the intermediate formation of the perchlorate, which occurs when pure potassium chlorate is heated slowly. For catalytic purposes, ferric oxide and manganese dioxide as well as cobaltic and chromic oxides are most effective. Decomposition takes place between 275° C and 475° C. The decomposition of chlorate is used for the generation of respirable oxygen, but an undesirable side reaction, *i.e.*, the formation of elemental chlorine, must be suppressed. This can be accomplished by the addition of a few percent each of barium peroxide and fine steel wool to the mixture[70].

Potassium Nitrate

It is not possible to say when or where potassium nitrate (saltpeter) was discovered; classical Greek and Roman literature apparently does not mention the substance. The Chinese are believed to have possessed it since at least 650 A.D., and the Arabs probably learned the method of preparing it from Oriental sources. Some confusion occurs because early references to nitre, νίτρον, or (*Att.*) λίτρον may signify the carbonates of sodium and potassium, rather than the nitrates[182]. In many places, nitrates occur naturally in the soil in low concentrations. They are formed by oxidation of ammonia, which is a common product of the decomposition of organic matter. In a few cases relatively high nitrate concentrations may be found, as when ground water seeps through the walls of caves and evaporates to form a crust. Such crude or "grough" saltpeter is still not pure enough for pyrotechnic use, and must be refined by repeated boiling and recrystallization to remove chlorides, calcium nitrate and other impurities. Large-scale production of saltpeter was made possible by the use of potassium carbonate (potash) obtained from wood ashes. After hot-water extraction of nitrate-bearing earth, addition of potassium carbonate brings about a double-decomposition reaction, resulting in potassium nitrate and precipitates of calcium and magnesium carbonates. The liquid can then be filtered or decanted, and the clear portion evaporated until potassium nitrate crystals form.

As the demand for gunpowder exploded, the naturally occurring sources of saltpeter soon became exhausted. Most European countries established nitre beds which imitated the natural conditions required for nitrification of organic matter. Such pits typically included lime as well as straw, dung, urine and other organic waste. After a suitable period of time, the earth from these pits could be extracted as described above. Due to the strategic importance of this industry, it paid well but was also subject to certain restrictions: in Prussia, for example, saltpeter boilers were forbidden to emigrate[182]. Despite such precautions, by the eighteenth century, most nations had become dependent on East Indian saltpeter, a situation which continued through the middle of the nineteenth century. Discovery of large sodium nitrate deposits in Chile and Germany permitted less expensive production of saltpeter. Not long afterward came the process for oxidizing ammonia to nitric acid, which is the source of practically all the nitrate oxidizers sold today.

At the time of the American Civil War, the Union Army permitted no more than one part of chlorides in 12,000 parts of saltpeter to be used for rifle powder. Some high-grade sporting black powders contained as little as one part in 60,000[137a]. For most purposes, potassium nitrate is considered sufficiently pure if it contains less than 1/1000 of sodium or chlorides.

Potassium nitrate is inexpensive, readily available and non-hygroscopic. The emission from potassium is weak in the visible part of the spectrum, but the nitrate is not a desirable ingredient in most colored flames because of the large quantity of solid material produced on combustion. Because more energy is required to dissociate it, potassium nitrate does not produce as high a reaction temperature with a given fuel as do the chlorate and perchlorate.

Potassium Perchlorate

Potassium perchlorate, $KClO_4$, must be carefully distinguished from potassium chlorate, $KClO_3$. Misquotations happen easily and accidents can happen due to mislabeling or because of misreading of correct labels. Greater hazard and great reactivity are often erroneously imputed to compounds having the higher oxygen content, in this case, the perchlorate. As we have seen in the relevant section, chlorates are often more hazardous because of their lower heats of dissociation (which result in lower decomposition temperatures) and their lower melting points. The decomposition of chlorates is more easily catalyzed, and the instability of free chloric acid is another factor which may contribute to the greater reactivity and sensitivity of chlorates compared with perchlorates.

Potassium perchlorate is made by the electrolysis of sodium chlorate to sodium perchlorate, followed by the addition of potassium chloride which causes the minimally soluble potassium perchlorate to crystallize from the solution. It is a strong oxidizer at high temperatures, and is compatible with aluminum. With fine magnesium, it may be dangerous unless the magnesium is passivated with a dichromate treatment. Potassium perchlorate has some of the ability to deepen pyrotechnic flame colors that is seen with chlorates. Because of the need for greater ignitability characteristic of the chlorates, perchlorates are not as commonly used in fireworks stars. They *are* more commonly used in blue and purple compositions than in other colors, as the catalytic effect of copper compounds enhances the ignitability and burning rate. Potassium perchlorate is sensitized by red phosphorus, realgar, antimony trisulfide and sulfur, but not to the same extent as the chlorate. The reactivity is sufficient to make possible the use of perchlorates in report mixtures. The perchlorate is not as easily decomposed by acids as are chlorates. The catalysis of perchlorate reactions has been studied extensively as part of propellant chemistry.

Ellern[70] reports the use of potassium perchlorate as an oxidizer for the generation of sulfur dioxide without excessive heat output. This is accomplished by the admixture of cupric sulfate to a sulfur/perchlorate mixture, taking advantage of the endothermic nature of the sulfate reduction:

$$2\,S + KClO_4 \rightarrow 2\,SO_2 + KCl \qquad \Delta H = +142.5 \text{ kcal/mol}$$
$$2\,S + CuSO_4 \rightarrow 2\,SO_2 + CuS \qquad \Delta H = -\ 30.5 \text{ kcal/mol}$$

Such sulfur dioxide candles can be used as a fungicide, in gopher bombs (but see p. 328), or for the destruction of wasp nests.

Sulfur

Sulfur and other easily volatilized materials enhance the ignitability of pyrotechnic compositions. Sulfur lowers the ignition temperature, but because most of the reaction products are volatile, it lowers the heat of combustion.

When raw sulfur is melted for purification, it solidifies on cooling and becomes a crystalline solid, completely soluble in carbon disulfide. After grinding, such sulfur flour is the type used in most pyrotechnic compositions. On the other hand, if sulfur vapor is chilled to solidify directly from the gaseous state, a fine powder is obtained consisting of various molecular aggregates, part of which are insoluble in carbon disulfide. This is called "flowers" of sulfur and it always contains some acid. When used in pyrotechnic compositions, it may impart instability and for this reason should be avoided. Flowers of sulfur is commonly used in agriculture as a fungicide, as a therapeutic agent, and for fumigation. Its ready availability may cause it to be used inadvertently.

Sulfur may function as fuel or oxidizer, as can its analogs selenium and tellurium. Selenium and tellurium are not used in commercial or military pyrotechnics, partly because both are toxic and partly because in the case of tellurium in particular, ingestion of even minute quantities is accompanied by a foul odor on the breath.

Table 16-3. Comparison of Some Properties of Titanium, Zirconium, and Hafnium

Property	Titanium	Zirconium	Hafnium
Atomic Number	22	40	72
Atomic Weight	47.90	91.22	178.49
Specific Gravity	4.54	6.45	13.09
Transformation Temperature from HCP to BCC*, °K	1155	1143	2013
Melting Point, °K	1943	2125	2500
Boiling Point, °K	3562	4688	4876
Melting Point of the Oxide, °K	2143	2950	3063
Boiling Point of the Oxide, °K	4900	5300	5500
Metal Temperature at Pressure of 10^{-1} Pa, °K	1827	2424	2470
Heat of Formation of the Oxide, kJ/mole, 298 K	-945.2	-1094.6	-1113.7

* HCP = Hexagonal close packed
BCC = Bodycentered Cubic

Titanium, Zirconium and Hafnium

These three transition elements have so much in common that they may be considered together. They have gained in popularity in pyrotechnic formulations requiring the highest reliability, such as first fires, igniters and flare compositions. The metals combine high stability (*i.e.*, low aging tendency) with great ease of ignitability.[37, 73, 77] They are high in heat output, burn with long duration hot sparks (see the comments on pyrophoricity in Chapter 10) and for this reason, display excellent fire transfer properties. In fireworks, stars and salutes containing titanium are now common.

The metals are prepared by the chlorination of their silicates (*e.g.*, zircon) or the oxides (*e.g.*, rutile), followed by magnesium or sodium reduction (Kroll process). The product, metal "sponge," may be used directly for pyrotechnic applications after crushing and screening. Alternately, the sponge may be *hydrided* causing it to become particularly frangible, facilitating the crushing operation. After screening, the resulting hydride can be used as a pyrotechnic fuel or reconverted into the metal by heating in vacuum furnaces. The latter type of product can be pyrophoric and requires great care in handling.

Titanium is now commonly produced as a high-strength structural metal, commonly used in aircraft. Zirconium can be produced economically from domestic sources only as a byproduct of titanium production. Australia is the largest producer of zircon, which is used as a recoverable foundry sand. The

Table 16-4. Hazard Ranges of Zirconium Particles[27]

Classification	Range of Particle Sizes		Ignition Characteristics
	Minimum	Maximum	
Fine Powder		< 0.01 mm	Easily Ignitable
Fine Powder	> 0.01 mm	< 0.85 mm	Ignitable with high-temperature spark
Fine Chips	> 0.85 mm	< 1.36 mm	Flame Required
Coarse Chips	> 1.36 mm		Burns only with difficulty when hot

demand for zirconium (a corrosion resistant component in nuclear reactors) has not kept pace in the last decade with the production capacity, mainly because of the unforeseen drop in demand for nuclear grade (hafnium-free) zirconium. Because the production of hafnium (which has 44-fold greater neutron capture cross section than does zirconium) is directly tied to the production of reactor grade zirconium, the supply of hafnium has decreased. The situation is reversed for titanium, for which the demand has significantly increased in recent years. Consequently, titanium sponge price has increased faster than that of zirconium. It is expected that the relative price level of zirconium will continue to fluctuate widely, affecting its choice for some pyrotechnic or incendiary applications. At the same time, the availability of high purity, and smaller particle, material of reasonable price has very much improved in the last decade. Whereas historically, the adjusted price for the ore and the metal has been sharply downward, we can

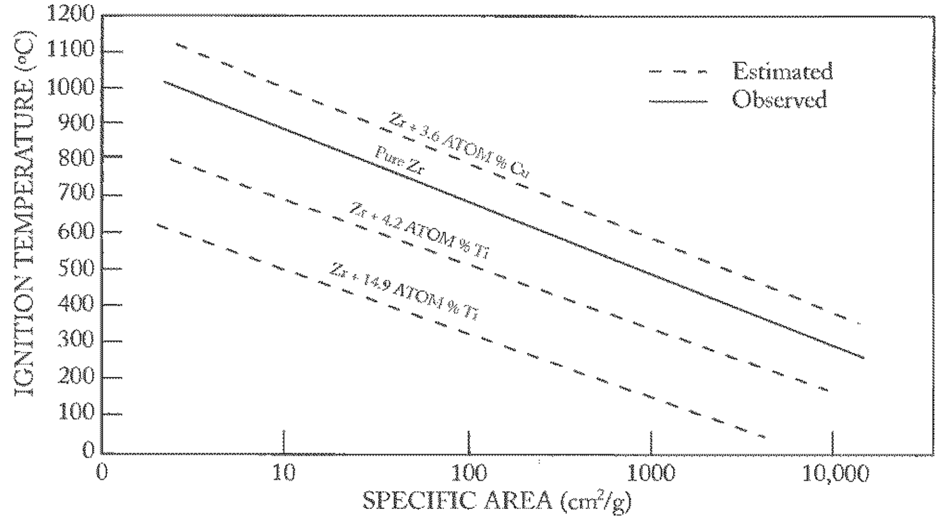

Figure 16-3. Dependence of ignition temperature of zirconium and selected alloys on particle size[207].

expect that the price of the metal will continue to be influenced by the cost of electric power.

Few data on the handling and ignition characteristics of hafnium powder have been obtained, and one may assume that they resemble those of zirconium. The hazards of handling and storing zirconium scrap frequently outweigh any savings to be gained by salvaging it. Such material is best disposed of by burning. Disposal of old or waste zirconium powder, which is packed either wet or dry in closed containers, presents additional hazards when attempts are made to open the containers. Particularly risky is the "digging" out of zirconium which may have settled. Whereas it is considered a safe practice to douse or flood zirconium "fines" with at least five times its weight of water, once the zirconium has settled and caked, one cannot really assume that the metal is still in contact with excess water. In this case the safest procedure is to burn the scrap. If this is not practical, an attempt can be made to dislodge the cake by prolonged tumbling of the containers. When zirconium is wetted with water, an oxide layer (see below) is formed, which protects the particles from further oxidation. Unless the water is present in excess, the initial heat may be sufficient to boil off the moisture locally and so trigger a run-away reaction.

Commercially-procured zirconium is frequently non-pyrophoric. This apparent inertness is due to partial hydride formation through contact with the ambient humidity. Such powders can be activated by gentle heating *in vacuo* at about 200° C. Care must be taken to allow all metal powders which have been so treated to cool to room temperature before further handling is attempted. Zirconium powder, for example, may be so reactive as to require storage in an inert atmosphere (but not nitrogen, with which it reacts to form the nitride).

The literature on zirconium combustion is extensive. When the burn time of the particles is plotted versus the particle diameter on log-log paper, a straight line of gradient 1 is observed for particles below 20 μm, and of gradient 2 for larger particles. A gradient of 1 is said to describe a "cubic" rate law (*i.e.*, one for which the burn rate is proportional to the particle size) and which is deemed to be kinetically controlled. A gradient of 2 describes a "parabolic" rate law, one which is diffusion controlled[207].

None of these metals is toxic. Titanium is not considered hazardous to handle, although ordinary care should be taken to prevent dust explosions when handling the commonly available 1-5 μm finely divided grades. Numerous instances of spontaneous ignitions of zirconium powder in both open and sealed drums have been reported. Zirconium powder handling or processing operations such as grinding, washing, drying, screening, weighing, blending, etc., should be conducted under an inert atmosphere; nitrogen is not useful as noted previously. Likewise, containers should be electrically conductive, avoiding the use of glass or plastic jars.

The linear log-log plots of the reaction rate (measured by oxygen consumption) versus time often show discontinuities, or an increase in reactivity. It is postulated that this rate change is associated with a phase transformation in the protective film. The initial film formed on zirconium is the cubic polymorph of zirconium dioxide. When certain alloying elements are added which are soluble in alpha zirconium, the oxidation film consists of the metal oxide dispersed in the cubic zirconia. When the ionic radius of the additive differs greatly from that of zirconium, it may form a separate phase rather than be soluble. In this case, inclusion of foreign metal oxides within the zirconia may interfere with the adhesion of the oxide film and so increase the oxidation rate. Examples of elements which enhance the reactivity are Ti, Sn, Pb, Nb, Si, Pt, V, Mo, U, C and B. In general, elements which stabilize the beta phase (*i.e.*, cause the BCC phase to be stable below the transformation temperature) tend to reduce reactivity. Examples are Co, Cu, Ni and Fe. Some of these speculations may appear to be removed from the subject of pyrotechnics, but insights gained in the solution of this problem may aid in improving the reactivity of pyrotechnic components.

Chapter 17

Generation of Light

Principles of Radiometry and Photometry

Distinctive light effects have been one of the chief aims of pyrotechnists throughout history. Development of new techniques and the availability of new chemicals have greatly improved pyrotechnic light production for military uses as well as for fireworks. By 'light' we understand not only the narrow spectral range of radiation that constitutes visible light (400-780 nm wavelength) but also the adjoining portions of the spectrum, ultraviolet (UV) and – even more importantly – infrared (IR). Sensing devices that respond to invisible wavelength emissions make it possible to utilize such radiation from a flare for a variety of tactical uses (Photo 17-1).

Our discussion of electromagnetic radiation starts with the concept of a "black body." A black body radiates energy in proportion to the fourth power of the absolute temperature. An emitter of visible light benefits twofold from an increase in temperature: the total amount of radiant energy output rises exponentially and the peak of the output function is shifted to shorter wavelength emission.

Table 17-1 lists the subjective color impressions from heated solids and their corresponding temperatures, but as will be shown, such impressions are not a reliable indication of the 'true,' *i.e.*, black body temperature, because radiant emission depends on emissivity, and because under certain surface conditions, the spectral temperature can be very far removed from the black body temperature.

Table 17-1. Visual Temperature Phenomena

Temp., °C	Subjective Color	Melting Point of Various Materials, ° C	
480	Faint red glow	Zinc	419
500 - 650	Dark Red	Antimony	630
650 - 800	Increasingly Red	Aluminum	660
800 - 1000	Bright salmon red	Silver	961
1000 - 1200	Orange to yellow	Gold, copper	1063; 1083
1200 - 2500	White	Nickel, platinum	1453; 1769
2500 - 3000	Dazzling white	Iridium, tungsten	2430; 3400

Before we enter the area of actual observation of radiant energy from flames, we must realize that the black body model is a very crude one at best. The first refinement is the concept of a grey body which emits energy in the same proportion as does a black body, but reduced by a constant fraction, *viz.*, the "emissivity," which is assumed to be independent of temperature. This model is an important one in that it permits the use of pyrometers and other types of radiometers for the determination of temperature from the radiant heat or light output. Another important exception to the black body arises from the fact that certain surfaces, especially those of refractory oxides, emit greater fractions of the total energy within discrete spectral ranges than one would expect on the basis of the temperature alone. This phenomenon is termed "luminescence". The various spectroscopic and physical units are tabulated in Table 17-2 as defined by the Illuminating Engineering Society of North America[118]. Some recommend that the English units and the older units dealing with "candlepower" be abandoned completely. Table 17-3 lists some conversion factors.

It may be helpful to see the units incorporated in an illustrative example. This one is based on Douda's data[65] from whose paper the test conditions and findings have also been obtained. The object of the experiment had been to explore the mechanism responsible for the large luminous efficacy of the magnesium/sodium nitrate illuminating flare. The test flares were composed of a mixture of 57% magnesium, 38.5% sodium nitrate and 4.5% polyester binder. A mass of 6.1 kg was compressed into a 10.9 cm diameter by 40 cm long cylinder which burnt cigarette-fashion for about 190 seconds with a flame 1.2 m long and 0.75 m diameter. The spectral radiant energy measurements were performed by focusing the radiation on a rapid scanning spectrometer. To estimate the spectral radiant energy, the image of the flame was reduced to the size of the monochromator slits. A mask defined the area over which the radiant energy was measured. Because the distance between the flame and the spectrometer was large (44 m) the radiant flux density was computed using an inverse-square distance relationship.

The problem of relating the true flame area to the observed flame area by photography was examined in detail by Blunt[21] who used narrow band filters and photographic film having multiple speeds in an attempt to quantify the radiant energy. He found that photographic methods are fraught with difficulty because the radiant intensity of flares depends on the electron excitation (a function of pressure, stoichiometry, and the location of the flame region under investigation) and on the depth and size of the flame. For this reason, Douda[66, 67] and Dillehay[46] have relied on radiometry for their studies of flare flames. When the sodium in the flare composition is replaced with other alkali metals (as for infrared illumination[152]), the flames appear to be smaller, but as compared to a sodium flare, they produce almost twice as much energy in the infrared region[21]. Therefore, flame studies by photography require a film sensitive to the spectral range of interest. Blunt[21] attempted to find a relationship between radiant energy, burning rates, flame area and luminous exitance, but did not succeed. His reports do not include the flare compositions except for an early study[22] which dealt with the

Table 17-2. Standard and Defining Equations for Fundamental Radiometric and Photometric Quantities[118]

Quantity	**Symbol**	**Defining Equation**		**Units**
Radiometric units				
Radiant Energy	Q	$Q(e)$		J
Radiant Energy Density	w	$w = \frac{dQ_e}{dV}$		$\frac{J}{m^3}$
Radiant Flux	Φ_e	$\Phi_v = \frac{dQ}{dt}$		W
Radiant Flux Density				
Radiant Exitance	M_e	$M = \frac{d\Phi}{dA}$	leaving a surface	$\frac{W}{m^2}$
Irradiance	E_e	$E = \frac{d\Phi}{dA}$	arriving on a surface	$\frac{W}{m^2}$
Radiant Intensity	I_e	$I = \frac{d\Phi}{d\omega}$		$\frac{W}{sr}$
where ω = solid angle through which flux from point source is radiated (steradian)				
Radiance	L_e	$L = \frac{d^2\,\Phi_e}{d\omega\,(dA\cos\theta)}$		$\frac{W}{srm^2}$
where θ = angle between line of sight and normal to surface considered				
Photometric units				
Luminous Energy	Q_v	$Q_v = \int K_{(\lambda)}\, Q_e\, \lambda d\lambda$		lm-s
Luminous Energy Density	w_v	$w = \frac{dQ_v}{dV}$		$\frac{\text{lm-s}}{m^3}$
Luminous Flux	Φ_v	$\Phi_v = \frac{dQ_v}{d\,t}$		lm

Table 17-2. Standard and Defining Equations for Fundamental Radiometric and Photometric Quantities[118] (continued)

Quantity	Symbol	Defining Equation	Units
Luminous Flux Density			
Luminous Exitance	M_v	$M = \frac{d\Phi_v}{dA}$ leaving a surface	$\frac{lm}{m^2}$
Illuminance	E_v	$E = \frac{d\Phi_v}{dA}$ arriving on a surface	$\frac{lm}{m^2}$
Luminous Intensity	I_v	$I = \frac{d\Phi_v}{d\omega}$	cd
where ω = solid angle through which flux from a point source is radiated			
Luminance	L_v	$L = \frac{d^2\Phi}{d\omega\,(dA\cos\theta)}$	$\frac{cd}{m^2}$
where θ = angle between line of sight and normal to surface considered			
Luminous Efficacy	K	$K = \frac{\Phi_v}{\Phi_e}$	$\frac{lm}{W}$

Table 17-3. Illuminance Conversion Factors[163]

1 lumen = 0.001464 W/lm — Ratio between radiant and luminous flux at the wavelength of maximum luminous efficacy.
1 lumen-hour = 60 lumen-minutes
1 footcandle = 1 lumen per square foot
1 watt-second = 1 Joule = 10^7 ergs
1 phot = 1 lm/cm^2
1 lux = 1 lm/m^2

	footcandle	lux	phot	milliphot
footcandle	1	0.0929	929	0.929
lux	10.76	1	10,000	10
phot	0.00108	0.0001	1	0.001
milliphot	1.076	0.1	1000	1

spectra of flames from the reaction of alkali and alkaline earth perchlorates with magnesium, aluminum and boron. For a comparison of the radiant flux spectra of sodium and potassium flares as function of pressure, the reader is directed to a report by Douda[63]. Blunt[21] has determined the radiant output as function of pressure for a sodium nitrate flare to be as follows:

$$
\begin{aligned}
I &= 1.84\,P^{2.16}\ \mathrm{W/sr} \\
\Phi &= 4.6 \times 10^4\,P^{0.35}\ \mathrm{W\ for\ P\ in\ Pa}
\end{aligned}
$$

Whereas this observed reduction of radiant flux with altitude is a well known phenomenon, the ratio of visible radiation to total radiation increases with altitude (*i.e.*, is shifted to the shorter wavelength) because the fraction of luminous flux from the excited sodium atoms increases, and the benefit of non-stoichiometric (fuel-rich) compositions decreases.

In Douda's studies, the total radiant energy was obtained by integration of the measured output over the wavelength range, and was found to be 1×10^7 J. The luminous energy was obtained by multiplying the output by the luminous efficacy of 630 lm/W* and found to be 2.8×10^9 lm-s.

The enthalpy of the flare reaction lies between 8.4×10^3 and 1.3×10^4 J/g where the lower limit is for the stoichiometric reaction:

$$6\,Mg + 2\,NaNO_3 \rightarrow 6\,MgO + 2\,Na + N_2$$

and where the upper limit includes the augmentation due to the admixture of air.

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* The so-called "mechanical equivalent of light" at the wavelength of maximum luminous efficacy. This value must also be corrected by the C.I.E luminous efficiency function over the wavelength range of interest.

Table 17-4. Luminance and Luminous Efficacy of a True Black Body at High Temperatures

Temperature, °K	Luminance, cd/m^2	Luminous Efficacy, lm/W
1600	2	0.2
2000	44	1.5
2200	130	3.3
2400	350	6.6
2600	779	9.4
2800	1,552	13.9
3000	2,872	19.2
3500	9,432	34.7
4000	23,400	50.3
5000	84,100	74

Therefore, the total energy liberated is 7.4×10^7 J during the 190 s burning period. By comparing this value with the measured output in radiant energy of 1.0×10^7 J we conclude that ≈15% of the total flare energy is radiated by the resonance line continuum. Dividing the luminous energy by the burning time, we obtain the luminous power of 14.6×10^6 lm; likewise, the total power dissipated by the flare is 3.9×10^5 W. These values translate into a luminous efficacy of 37 lm/W at a flare temperature of approximately 3000 K* (see Chapter 7). Table 17-4 shows that the luminous efficacy of a black body at 3000 K is less, namely about 19.2 lm/W. Douda[66] has shown that this augmented luminous power can be accounted for by radiative transfer of emission from the sodium resonance line, and that there are corresponding regions of lower emissivity at longer wavelengths. This means that the sodium flare (and, as we shall see, other alkali metal flares) derives the main portion of its luminous power from a broadening of the resonance line, a phenomenon which is a function both of pressure and temperature.

The Mechanism of Illumination by Flares

A recent dissertation by Dillehay[46] has extended Douda's work on sodium flares to those containing other alkali metals, and moreover has placed Douda's work on a broader phenomenological base. Dillehay's model took into account the effects of stoichiometry, admixture of air, heat loss along the flame axis and the effects of altitude (pressure). His findings are summarized as follows:

> As the fuel and oxidizer react, the combustion products are expelled from the surface and form a gaseous volume that radi-

---

* Other parameters of interest are computed as follows: the *gravimetric luminous energy*, obtained by dividing the luminous energy by the mass of material reacted, lm-s/g, and by dividing by 2π obtain it in candelas (lumens per steradian): cd-s/g, and to obtain the *luminous exitance* of the flame in lux, (lm/m^2), divide the luminous flux (lumens) by the superficial flame surface.

ates both line spectra and a continuum due in part to radiative transfer broadening and in part to greybody emission from the solid particles in the plume. The burning rate of the composition can be optimized by tailoring the particle size of the magnesium fuel. If the rate is less than optimum, heat losses will be excessive and a low light integral will be recorded. If the rate is too high, material will pass the reaction zone too fast for attainment of equilibrium and material will be lost to the reaction and so result in a low light integral as well. As the flare formulation is adjusted to be fuel rich, the excess fuel reacts with air and the reaction proceeds further along the plume axis to give a longer plume. The plume length is also a function of altitude in that at reduced pressure, the plume expands along the axis resulting in a longer plume. Likewise, the length of the plume increases with increase in flare diameter because it takes longer for the plume to mix with the air.

Illuminating Flares

The visible spectra of red, green and yellow flares used by the Navy were published by Webster[248]. Measurements of the dominant wavelength, purity and luminous flux were made with a tristimulus colorimeter. The composition of these flares is shown in Table 17-5.

The opposite effect, namely low luminous output in the visible region, is achieved using organic fluorine compounds such as polytetrafluoroethylene as oxidizers. These compositions, as well as those containing alkali metals other than sodium, are of use as illuminants when the terrain is viewed with infrared detectors. Table 17-6 lists the compositions of various near infrared flare compositions[152]. Infrared detectors take advantage of the fact that natural ground cover is a particularly good reflector in the infrared region,[169] whereas man-made but camouflaged objects become visible by contrast. A special type of flare is the thermal decoy which has a strong emission in the infrared range. Decoys may utilize the magnesium-fluorocarbon reaction to form hot carbon particles as the

Table 17-5. Navy Flare Compositions[248]

	Red	Green	Yellow
Magnesium	24.4	21.0	30.3
Potassium perchlorate	20.5	32.5	21.0
Strontium nitrate	34.7	-	-
Barium nitrate	-	22.5	20.0
Polyvinyl chloride	11.4	12.0	-
Sodium oxalate	-	-	19.8
Copper powder	-	7.0	-
Asphaltum	9.0	-	3.9
Laminac	-	5.0	5.0

Table 17-6. Near Infrared Flare Formulæ[152]

Component	760 nm	790 nm	800-900 nm
Silicon	10	10	16.3
Potassium nitrate	70	-	-
Cæsium nitrate	-	-	78.7
Rubidium nitrate	-	60.8	-
Hexamethylene tetramine	16	23.2	-
Epoxy resin	4	6	5

source of radiant energy. Table 17-7 lists the equilibrium composition of such a magnesium-fluorocarbon reaction at 1200 K[233].

Pyrotechnic light production has two military purposes: illumination and recognition. Illumination for photographic purposes is best achieved by very brief high-intensity flashes of light. Signalling by white light, while important in certain spotting charges, is less common than signalling with colored flames, while the use of white and colored light for amusement is of importance in fireworks.

High-intensity, long-burning white parachute flare candles are used to illuminate large areas of ground for the purpose of target illumination, illumination of combat areas, as anti-infiltration devices or in aiding in emergency landings of aircraft.

The light of a full moon on a clear night approaches an illuminance on the ground of 0.26 lm/m^2 which may be considered to be the minimum useful light intensity for military operations, whereas an intensity one order of magnitude greater is usually thought necessary for night operations. To achieve this level of illuminance, 1 to 2 million cd are required for 2 to 3 minutes. This requirement is met by air-dropped flares as well as by smaller devices, such as those launched from howitzers or mortars, which are designed to operate at altitudes less than 2000 meters.

Castable Flare Illuminants

Much of the development of castable candle compositions dates from the 1960s[2] and therefore can hardly be considered new or recent, but represents in many ways the state of the art. Typical design, composition and performance characteristics of such a flare are as follows:

Table 17-7. Equilibrium Composition of Magnesium-Fluorocarbon Reaction Products (mole fractions)

$C_{(s)}$	0.45316	CF	0.00755	C_3	0.00485
MgF	0.03023	F	0.03197	CN	0.00224
CF_2	0.00206	C_2N	0.00118	N_2	0.01115
MgF_2	0.44743	C	0.00078		

NOTE: Adiabatic reaction temperature 3400 K. Trace species are not listed.

Table 17-8. Tamp-Cast Illuminating Flare[4]

Carboxyl terminated polyester binder		7.4
Epoxy curing agent		1.5
Magnesium, 50/200 mesh, HF passivated		61
Sodium nitrate,	42-62 mesh	10
	60μm average particle size	10
	5μm average particle size	10
Iron linoleate (catalyst)		1

Length	76 cm
Density	1.5 g/cm3
Weight	76 kg
Luminous intensity	$18x10^6$ cd
Gravimetric luminous energy	$46x10^3$ lm-s/g
Burn rate	0.23 cm/s

Advantages are seen in improved light output and greater safety due to the automated nature of the casting process. Even though many manufacturing steps are automated, the total operation continues to be quite labor intensive. This is because lot sizes, while typically numbering in the thousands, are still not sufficiently large to justify the use of robotic equipment. The performance testing of candles in terms of safety and reproducibility owes much to the techniques developed in solid propellant studies[4]. Hence, test parameters are obtained from standard JANAF or ASTM dog bone tensile specimens, or where applicable, from lap shear specimens, for the determination of modulus and strain parameters. Burning rate characterization, by contrast, is always performed on an entire flare.

A specific study of castable material for flares was performed by Waite and Arikawa[9, 244] using sodium perchlorate as the oxidizer. Commercial polyester resins generally were found to contain styrene and therefore were low in oxygen content. Desirable binder properties include a minimal carbon content to reduce the formation of elemental carbon in the plume, and that the binder be castable and polymerizable at room temperatures. As the amount of binder is increased, especially the amount of carbon, the gravimetric luminous energy is decreased.

Safety in Flare Manufacture

The manufacture of magnesium flares or candles is among the most hazardous in pyrotechnic practice. Consequently, the operations are conducted with relatively small numbers of devices resulting in a highly labor-intensive operation. If the materials are mixed in such a manner that fuel and oxidizer come into contact before at least one of them has been thoroughly admixed with liquid binder, the hazard of ignition by friction or by static discharge is greatly increased. For this reason the preferred sequence of mixing is to combine the metal powder and the binder first, diluted sometimes with a volatile solvent such as acetone or methyl ethyl ketone. The older literature mentions trichloroethane but the current trend of blaming half the world's ills on chlorinated hydrocarbons has probably made this practice a thing of the past. Whereas at one time the last step in the pressing operation consisted of pressing first fire onto the mixture, the current practice is to paint it as a slurry onto the exposed surface.

During development of new formulations and during test burns, as part of the quality control procedure, particular attention is paid to any tendency toward grain cracking or grain-case separations as these may lead to explosions. Because complete control over all conditions in and around mixing installations is not attainable, potential damage is limited by shielding and barricading. Complete automation, in terms of the use of robots, is conceivable but at present is not economically feasible because of the small lot sizes.

Photoflash and Flashbulbs

Loose powder mixtures of fuels and oxidizers can react with explosive force. Because the entire process may take place in milliseconds, the luminous intensity from such events is very high, on the order of 10^9 cd, with luminous energies on the order of 10 to 30×10^6 lm-s. This phenomenon is relied upon for the illumination of the ground at long distances and over large areas for the purpose of photographic reconnaissance. Photoflash powders are loose mixtures of powdered oxidizers such as barium nitrate and potassium perchlorate with metallic fuels such as flaked aluminum. They can be initiated with a centrally placed explosive charge. Photoflash compositions containing hafnium, cerium, titanium and zirconium with potassium perchlorate have been studied in Australia,[251] but otherwise little research has been performed in this area for more than twenty years, and photoflash bombs are becoming a thing of the past. The RF4 reconnaissance aircraft and some old Navy planes were the last to have dispensers to launch photoflash cartridges. They are now all out of inventory and in mothballs. Hence, photoflash items are not in use by United States armed forces; M112, M112A1, M123, and M123A1 photoflash cartridges and M120 and M120A1 photoflash bombs are now in an obsolete category, and those that are left are awaiting disposal. There are no plans to develop replacements.

Until recently, photoflash bulbs were a device of major importance in photography. There were two kinds: one which consisted of fine aluminum or zirconium ribbon within a glass bulb containing oxygen at reduced pressure, the flash being set off electrically; the other, pyrotechnically-actuated flash cubes. The mechanism was as follows (US Patents 3,535,063, 3,540,913 and 3,674,411). An initiating composition was coated on a wire which was centered in the cube, the wire acting as an anvil for a percussion initiating action. When the picture was taken, the shutter button pushed up the flashcube pin which lifted a torsion spring from its latch so that its free end struck the initiating composition. A typical mixture contained approximately equal quantities of boron, zirconium, red phosphorus and potassium chlorate. During the combustion of zirconium, 1700 lm-s/cm^3 are emitted when burned in an atmosphere of oxygen, which is 1.7 times the luminous energy density of aluminum. In theory, the performance of hafnium would have been even better owing to the high stability of hafnium oxide at lower pressures.

Production of White Light

General Remarks

Pyrotechnic light production has two purposes: illumination and recognition. In other words, it is important either to light up an object or an area to make it visible to the eye or to a camera; or it is desired to see or scan by instrument the light source itself as a signal and, in the case of fireworks, as an æsthetic design of light.

The major part of this discussion will be devoted to high intensity, long-burning white parachute flare candles, which are used to illuminate large areas of the ground for the purpose of showing bomb targets and bomb damage at night, illuminating combat areas, acting as anti-infiltration devices, or aiding in emergency landings of aircraft. Points treated will be the optical requirements, types of hardware, chemistry of compositions, and techniques and allied problems of manufacture.

Optical Considerations

If we restrict our requirements to the (geometrically) normal aspect of light to target, not involving the cosine law with regard to hilly ground or angle of light to ground, the required luminous flux density, assuming identical atmospheric conditions, will depend on the height of the flare above the target. Since a parachute flare descends, but renders in normal practice a fixed light output during its burning, the most unfavorable – *i.e.*, highest – point of the flare above the ground determines the minimum output needed. For the minimum illumination required (0.27 lm/m^2), a flare of 1 million candelas will satisfy this requirement from an altitude of 1300 m and for a 1700 m operational radius. After a drop of 600 m, the optimum radii would be 1300 m for 0.5 cd and 850 m for 1 cd. More details on formulæ and charts for illumination can be found in a Picatinny report[169].

The gist of this thumbnail sketch is that a luminous intensity of one or two million cd over a burning time of 2 to 3 minutes is needed for many operations. Air-dropped parachute flares of this size exist, as described below, as do smaller less powerful units.

Chemistry of Illuminants

Based on theoretical considerations, we may postulate that a flare of superior white light output should have the following characteristics:

1. The major fuel-oxidizer reaction should produce the highest possible heat output per unit volume of compressed composition;
2. The heat of combustion in air of excess fuel should be high;

3. The melting and boiling points of the products of reaction should be high and their decomposition temperatures should lie above their boiling points;
4. The solid refractory main product (oxide) should disperse readily in air. No sintering of particles should occur near the reaction zone;
5. Volatile reaction products or by-products should be present in sufficient quantity to carry away the reaction products from the reaction zone, but ingredients that tend to convert refractory products into vapor should be absent;
6. Emission characteristics should be optimal for the visible part of the spectrum and luminescent phenomena must contribute to maximum emission of visible radiation.

Of all metal fuels investigated so far, magnesium best fulfills the rôle of the principal emitting source. It vaporizes in the reaction zone. Aluminum is less effective, though its caloric output is slightly higher than that of magnesium. Fine particles such as flake aluminum burn with great brilliance as do titanium, zirconium, cerium, uranium, and their hydrides. However, such particles tend to burn in the solid phase without evidence of vaporization. Vapor phase oxidation of aluminum can only take place at a temperature near its boiling point (2327° C), which is about 1200° C higher than that of magnesium (1105° C). When aluminum is preheated to 400° C, oxidation is continuous and 81-99% complete, while non-preheated system reacts in a pulsating manner as aluminum vapor periodically breaks through the oxide film covering the droplets of metal, leading to only 37-56% completion of the reaction. It may be mentioned that while powdered magnesium burns completely and in the vapor phase, as evidenced from its ash and flame formation, a burning magnesium ribbon will leave as much as 18% of unburned metal in the part of the ash that is sintered.

Since reaction products surround the flame as dense white smoke, a complex relation exists between smoke formation and light production. At the present state of the art, a superior white-light source cannot function without the presence of white smoke from magnesium oxide and other oxides (formed from nitrates). By reflection of the light, such smoke can have some beneficial effect, but of course it will be detrimental to illumination. The position of the flame, the ambient air currents, and the convective draft from the heat of the reaction combine to keep the flame visible or to obscure it. However, it has been indicated from theoretical consideration that the magnesium oxide within the flame itself is not opaque to visible radiation.

The choice oxidizer for high-energy white flares is sodium nitrate. It fulfills several important functions: the reaction with magnesium forms magnesium oxide; the heat of reaction per gram of components is high because of the high oxygen content of the nitrate and the low equivalent weight of the sodium; and the sodium exhibits luminescent properties that add significantly to the useful light production.

In older formulations, barium nitrate appears as the oxidant but with sodium oxalate added. Light output and other pertinent data for experimental flares containing both sodium and strontium nitrates in varying proportions have been the object of much study. White light is sometimes produced with barium nitrate to which is a much smaller percentage of strontium nitrate is added in order to neutralize any appearance of color. Lower-energy white lights, especially for fireworks, may also use potassium nitrate or chlorate.

Binders are added to the fuel/oxidizer mixtures to aid as internal lubricants while in liquid state during the compacting phase. Small additions of castor oil, linseed oil, or paraffin wax can be used. Shellac, rosin and other natural resins, resinates, stearic acid, or dextrin are found in many formulæ, especially for small items and fireworks. In large flare candles, materials of strong binding force, which solidify and bind by catalytic action without external heating, are now the preferred binders. The ones most often specified belong to the class of alkyd resins and are unsaturated polyesters that contain copolymerizing styrene monomer. The best known in pyrotechnic practice are manufactured by the American Cyanamid Company under the trade name Laminac. Other cold-curing resins such as epoxy resins can be used.

Consideration has been given to replacement of the envelope (casing) by other related materials such as plastics in lieu of paper, or light metals in place of steel. The former may have some advantage because of the greater strength and moisture resistance. Certain plastics appear also to contribute to light output, though indications are that such influence is restricted to flares of smaller diameters. As to the use of metals such as magnesium or aluminum as flare canisters, their low melting points preclude effective use of the fuel value of the envelope to contribute to light output. Such canisters simply melt away in irregular patches and expose the unburnt portion of the flare, rather than contributing effectively to light output through combustion.

The technical problems involved both with cardboard and steel cases include the question of loading. Under the conventional system of loading a powder mixture directly into the case and consolidating it by hydraulic pressure, it is necessary to subdivide the charge into several parts. As a rule of thumb, the height of the consolidated charge should be no larger than the interior diameter of the tube or shell. Shallower increments in larger numbers are often used. This adds to uniformity in compaction of the material.

Where the envelope is made of cardboard, there is not only a danger of bulging and breaking, but also the influence of friction in the cylinder wall, which causes it to collapse at the lower end in an "accordion" pleating that weakens the structure and shortens the tube length. The use of large, cumbersome, expensive, hinged split moulds and the consequent need for time-consuming handling adds greatly to the cost of loading such flares.

With steel-cased flare candles, the loading is somewhat simplified because of the rigidity of the metal case, but other problems arise. The direct contact of metal wall and composition may lead to erratic burning as a result of the heat conductivity of the metal. In addition, cracks, insufficient bonding, or contraction may create accelerated burning with build-up of pressure, which can result in actual explosion of the candle. The most unfavorable conditions exist when a center post increases the possible areas where flaws may occur and when the burning rate of the composition is particularly high.

Swabbing the inner surface of the metal canister with a catalyzed Laminac solution, giving it time to convert to a thin protective coating, helps prevent erratic performance of standard illuminating canisters.

As a rule, loading pressure for all military items is as high as practical. By maximal compaction, the largest amount is packed into the smallest space with justifiable expectation of greater efficiency; the effects of sudden acceleration, deceleration, vibration, or temperature variations might also be minimized. However, other considerations include lowered ignitability, the stresses exerted during pressing on the casing, and the proven possibility of the break-up of larger crystals (350 µm) at 700 kg/cm^2 with consequent effects on burning. Therefore, the compaction pressure for large candles does not exceed 700 kg/cm^2. It takes little arithmetic to calculate that even below this limit a large flare needs a 60-ton press.

Specific Hazards of Production of Large Flares

The nature of the chemicals involved in high-powered flare compositions and the large amounts processed at one time create specific hazards, some of which have been assessed only after grievous experiences. Unfortunately, such experience is rarely shared, analyzed, and critically evaluated.

The large particle size of the magnesium in the flare formulæ discussed above, the relative inertness of nitrates (compared with chlorates and perchlorates), and the large amount of liquid resin having friction-reducing (hence phlegmatizing) character should make the flare formulæ among the safest. Instead, open trough-type mixers (mix mullers) with moderate charges (less than 25 kg) have blown up with explosive force. Flares in moulds in the process of compaction have broken moulds and damaged pressing equipment, and burning flares have exploded during tests with serious consequences.

In some of the cases, a reason can be given for the most likely causes of accidental ignition. If the sequence of addition of materials to the mixer is such that fuel and oxidizer come in contact before at least one of the two has been thoroughly mixed with liquid binder, the hazard of ignition by friction or by another obscure cause is greatly increased. For this reason, the preferred sequence of mixing is the combination of metal powder and binder, the latter sometimes diluted with a volatile solvent such as acetone. Though there may be some qualms about addition of a highly flammable or potentially reactive solvents, the advantages of fast and uniform wetting of the magnesium together with the high volatility of the solvents may outweigh the more remote hazards and other disadvantages of resins. Residual solvent strongly inhibits the hardening reaction of some resins.

One case of an explosion in the mould occurred during the last pressing, after the first fire had been added. Any accidental ignition due to excessive friction, as might occur when steel canister and pressing ram are not perfectly centered, would of course be easily explained when the more friction-sensitive first fire is involved. Such hazard is greatly lessened by a reversal of the pressing procedure, starting with the first fire, but this is often impractical and is impossible where a permanent bottom closure is present.

While these findings are valuable, they should not detract from the point that fuel/oxidizer mixtures can deflagrate explosively in a loose or compacted state and not necessarily in what may be called confinement. The rapidly released gases or gasified solids, under a self-accelerated burning rate and pressure build-up, make the term confinement meaningless for more than minimal, thinly-spread quantities. Because complete control over conditions in or around a mixing installation is beyond human ability, a potential explosion must be made harmless, at least to life and limb of personnel, by proper shielding and barricading, and other safety precautions. Complete automation would be impractical (though it can be achieved for simpler processes such as making photoflash bombs), and a satisfactory compromise approach can be reached that permits the direct handling of the completed mixture (subdividing, weighing, loading into the mould) without undue hazard.

The explosive deflagration of flares during burning, especially of experimental variations or new items, is in some respect a more serious problem because it is less common and is not expected to occur at all.

White Signals

Visual signals may indicate the location of an item in flight or at the target, or they may constitute a distress signal or a prearranged message. Pyrotechnic light signals are normally designed for night use, in which case their luminous intensity need seldom be high. For daytime use, however, in order to achieve a contrast against the sky, as in missile tracking, a luminous intensity of 100,000 cd or more is needed. This suffices for small missiles such as the Sidewinder or Bullpup, which employ tracking flares. For tracking at high altitude, flash charges are preferred, as shown in the next section.

Enhancement of radiation from the propellant exhaust of drones by target flares may be considered "visual" signalling even though it is only for the benefit of a sensor in an attacking missile guided by infrared radiation.

A peculiarity of both tracking and target flares is their preferred mode of initiation, *viz.*, by fire transfer from the hot propellant gases. This is called "parasitic ignition."

Spotting charges may be designed both as day and night signals combining light and smoke formation.

Quantitatively, the most abundant use of pyrotechnic signals is probably in tracers for projectiles. Since most tracer formulæ pertain to colored flames, this whole subject will be treated separately.

Testing of Flares

The measurement of the luminous intensity of a flare is not a difficult procedure. It requires the erection of a test tunnel painted a flat black color on the inside and provided with baffles to prevent excessively high readings because of reflected light entering the barrier layer-type light-sensitive cells. The "fireplace," where the candle is burned, is painted white – a condition easily maintained because of the copious deposits of magnesium oxide from the flame. An exhaust fan eliminates obscuration of the flame by smoke. Provisions must be made for burning the flare in at least two vertical positions, flame up or flame down. Since the light output (and burning time) of illuminating shells varies greatly with the spin of the projectile (at 3000 rpm the burning time is reduced to one-half), a turntable may be required to simulate operational conditions.

In order to bring the photocell to a response that approximates the sensitivity of the human eye for the different parts of the visible spectrum, color-correcting filters are interposed that attenuate the ranges in which the selenium cell normally used is more responsive than the eye, *i.e.*, below 5300 Å and above 5800 Å wavelength. Standard lamps are used for calibration.

The procedures are not claimed to measure accurately the actual luminous intensity but rather to permit a fairly precise measurement of approximate values for purposes of routine checks and for acceptance tests. More elaborate are the provisions if one is specifically interested in the spectral quality of the light or in nonvisible portions of the spectrum. By use of a multiplicity of optical filters with several photocells, or by use of other sensors such as lead sulfide and lead telluride cells or bolometers and cut-off filters, more information can be obtained. Only by use of a scanning device that permits a continuous variation of the wavelength for which output is recorded can a true picture be obtained. Monochromator spectrometer data are discussed in an NAD Crane report[52], which also features a graph relating radiant energy vs. wavelength for a pyrotechnic flare, compared with graphs for various non-pyrotechnic light sources.

Flash Charges

Many fuel/oxidizer mixtures can react with explosive force under conditions leading to self-acceleration of an initially slow and orderly reaction. Pressure build-up is the primary accelerating factor. It may take place with consolidated charges, not necessarily in complete confinement, if cracks or defective bonding precipitate a reaction rate at which the gases cannot properly escape, whereupon the increased pressure leads to still faster reaction – a cycle completed in milliseconds. The same may occur – in fact is far more likely to occur – with loose powder mixtures. If such an explosive reaction and dispersion is the desired effect, confinement of the charge alone is not relied upon, but an explosive stimulus is applied from a central burster; if the charge is large, a certain amount of black powder will help in uniform formation of a fireball. Since all the energy of the reaction is liberated in less than one tenth of a second, the luminous intensity from a properly formulated flash charge is very high. Illumination of the ground from a large distance and over a large area can be achieved for the purpose of photographic reconnaissance. Smaller flashes are suitable as signals and for close-range photography.

Illuminating Flashes

Illumination for photographic reconnaissance at night in wartime is accomplished with powder mixtures or, exceptionally, by metal powders alone dispersed in air by an explosive charge. Depending on the altitude at which the unit is released, a relatively small "cartridge" or much larger "bomb" is used.

The luminous intensity from a flash charge observed with proper instrumentation measuring output *vs.* time will rise steeply and decay rapidly. For the M112A1 Photoflash Cartridge, the following data have been obtained: time to peak 2.2 ms; after 15 ms, output half of peak; after 28 ms, only one-tenth. Generally, the useful light output is measured by integrating the output *vs.* time curve over the first 40 ms. From the viewpoint of coördination of a flash with the ærial camera, a minimum time to peak and reduced burning time for the period of adequate light emission are desirable goals for further improvement.

Because of the destructively explosive force of the flash powder, the cartridge must be ejected from its dispenser and not exploded before a certain minimum time has passed. The M112 cartridge was furnished with delays of 1, 2 or 4 seconds; the larger M123 with 2, 4, or 6 seconds. As with flares, the figures in older manuals regarding output, loading density, etc. may be lower than achieved in more recent times, although not very much effort has been expended on this subject in many years. In addition, the reported figures contain some obvious misprints or errors and the delay-time variation, *e.g.*, of the 1-second delay, has been improved from an earlier +0.3s to +0.1s. This, however, is still regarded as excessive and complicates the shutter synchronization problem. Photoflash bombs rely on mechanical fuzes.

Aerial night reconnaissance photography was started by the British in 1918 and went through numerous phases because of the difficult synchronization of illumination with camera action. During the course of development, the preferred materials were magnesium, aluminum, or magnesium/aluminum alloy with the oxidizers barium nitrate and potassium perchlorate. The metal alloy was used in World War II because of the severe shortage of powdered aluminum and magnesium, the latter being laboriously produced by a modified lathe-cutting operation that was woefully inadequate to provide the smaller particle sizes. The alloy, on the other hand, is a brittle, relatively easily comminuted solid. A typical photoflash formulation consists (today) of 40% aluminum (20 μm), 30% barium nitrate (147 μm), 30% potassium perchlorate (325 mesh), and the autoïgnition temperature is typically 760° C.

The luminous efficiency in terms of cd-s/g metal for flash charges is much inferior to that for flares. Since a much larger part of radiant emission is in that part of the infrared range that can be made photographically useful with special IR sensitive film, efforts have been made along these lines.

Another decrease of efficiency occurs when only metal powder without oxidizer is dispersed. The latter type, the so-called "dust bombs," were developed because large amounts of explosive flash mixture make the æroplane carrying photoflash bombs extremely vulnerable to destruction. The flash charge may explode when the bomb is perforated by bullets or shell fragments, destroy everything in its vicinity. Bombs that contained only metal powder used either aluminum powders or (in this country) a magnesium/aluminum alloy (65:35).

The use of metal powder alone causes a longer time to peak light output than is seen with regular flash powder. The inefficiency of the dust bombs led to development work on segregated compartments for fuel and oxidizer, both surrounding the burster coaxially. However, these efforts did not lead to a better utilization of the powder.

The problems encountered in the creation of a fireball from a flash charge, its development, duration, size, shape, and useful light output, depend on many factors and are undoubtedly even more complex than the problems of ordinary pyrotechnic flames. Chemical ingredients, geometry of the total assembly, the quality of the burster, and the degree of confinement of the charge (*i.e.*, the strength of the container and its seals) prior to the burst all having a bearing on performance. The subject has been treated in great detail in the Military Pyrotechnics Series[169].

Because photoflash powders are hazardous in any quantity, one might regard their processing and the manufacture of cartridges and bombs as some of the most hazardous tasks in pyrotechnics. It is just this definite, unequivocal danger that leads to such extensive precautions and special management so that the hazard becomes greatly reduced. One safety factor lies in the possibility of mixing the ingredients, either in the final containers by vibration or with the help of an attached canister or mixing device, and of disconnecting the two units by remote control only after the mixed powder has come to rest in the cartridge or bomb. This makes the production actually safer than that of flares where loose powder has to be handled after mixing by pouring, pressing, etc., with only partial remote control action.

Signal Flares

The majority of flash charges used as signals or imitations of the flash from a weapon are relatively small. They comprise those that are incorporated in training weapons, such as the M110 Gunflash Simulator used for the training of artillery observers and troops in manœuvres. This item is also used as a decoy, since its effect closely resembles the flash of certain guns. The M115 Projectile Ground Burst Simulator, and several air-burst simulators fired from grenade launchers or pistols are described in Chapter 21 on generation of sound.

Flash charges are also used to indicate the point of impact of practice bombs, and also of small caliber spotting rounds shot from a small arms weapon with a trajectory identical to that of a larger gun. Formerly, black powder was used for such purposes, providing both flash and smoke. Nowadays, a zirconium-based flash composition has been successfully employed, exhibiting 1.5 million candles and an exceptionally long duration (700 msec) when loaded in a 20-mm spotting round of about 6.5 cm^3 volume.

Colored Lights

This section will be devoted to colored lights used for military signalling and for civilian emergency flares, while the colored flames, flares, and spark effects of fireworks for pleasure have been treated separately in Chapter 15. The division is necessary because not only the choice of colors but also compositions and manufacturing techniques are different. Both branches can of course benefit from each other and some overlapping is obvious.

Color Selection

Colored signals must be recognized unequivocally and named as to the color they represent to all observers who are not color-blind. The color should not lose its quality when viewed from a long distance or under other unfavorable conditions such as though haze or in daytime. Fireworks, on the contrary, need neither be very luminous nor restricted to definable colors. They are viewed from conveniently close proximity on clear nights and delight the eye by a wide variety of delicate tints of, for example, pink, orange or violet, none of which would be suitable "red," coded as such.

Blue and purple cannot be regarded as satisfactory signal colors. Blue would be safe if the illumination were very high. Red is the ideal signalling color if orange lights are not also seen by the observer. Green is a safely recognizable color. Yellow and white are safely recognizable if used separately.

These views seem to be well applicable to pyrotechnic color recognition and identification problems. Red, green, and yellow are the foremost recognized signal colors, though one occasionally finds the designation "amber" and there are blue signal lights. The latter seem to be somewhat maligned and deprecated, apparently not so much on optical grounds as because it is difficult and perhaps impossible to create a brilliant blue pyrotechnic flame of great depth of color.

In a more limited way, a problem exists in the proper naming of colors and perhaps also in the bias of some observers with otherwise normal color recognition toward the color yellow, whereby the slightest admixture of yellow with blue, especially in light shades, causes the person to identify this color as "green" rather than "blue."

It is possible to extend the variety of color messages by combining several signals as simultaneously-seen discrete lights of the same or of different color.

Colored signals as ordnance or utilitarian commercial items include a variety of devices, displaying one or more "stars" which function either on the ground or more often by being propelled into the air from the ground. If of short duration these are unsupported, but if the burning time is longer, they are suspended from a small parachute. Such signals are useful for communication, identification, or as distress signals or spotting charges.

In compiling a list of compositions for colored flame production, formulæ have been taken from specifications for "stars." Stars are similar to flares except for the duration of the light (0.1-2 min), and the luminous intensity is less. Additionally, they are colors used primarily for day/night signalling. Star signals may contain a single star or a cluster of two or more.

Since there is now little overlapping between the formulæ for ordnance items and for fireworks, the latter are only of passing interest to the designer of military flares and stars.

Table 17-9. Selected Flare/Star Formulations[160]

	Green		Red		Yellow†		White	
Magnesium, 30-50 mesh	35	16.8	–	29	26	18	58	–
Magnesium, 50-100 mesh	–	16.8	29	–	–	–	–	–
Barium nitrate	22.5	40.1	–	–	29	17	–	–
Potassium perchlorate	22.5	9.5	9	29	23	17	–	–
Polyvinyl chloride	13	–	12	–	–	–	–	–
Linseed oil	–	–	–	2	2	3	–	–
Dechlorane	–	12.6	–	–	–	–	–	–
Hexachlorobenzene	–	–	–	4	5	12	–	–
VAAR*	–	4.2	–	–	–	–	–	–
Laminac	7	–	7	–	–	–	4.5	5
Gilsonite	–	–	–	2	2	–	–	–
Sodium oxalate	–	–	–	–	13	17	–	–
Sodium nitrate	–	–	–	–	–	–	37.5	53
Strontium nitrate	–	–	43	34	–	16	–	–
Aluminum	–	–	–	–	–	–	–	35
Tungsten	–	–	–	–	–	–	–	7
Autoignition Temp, °C	491	340	376	391	496	532	460	564

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* vinyl alcohol-acetate resin

† magnesium granulation is unspecified

Formulations for red and green flame are remarkably similar. The basic coloring agents for red and green are the elements strontium and barium, mainly in form of the relatively volatile chlorides. It will not do, however, to use the chlorides as such since the formula would simply be too "congested" if these salts were combined with a fuel/oxidizer heat source. In other words, there might not be enough of all three major ingredients, or, as one might say facetiously, the pyrotechnist is stumped by the fact that there are only one hundred percent in a formula. At least one chemical must therefore do double duty, and the best solution to this problem would seem to be to utilize as oxidizers the chlorates or perchlorates of strontium and barium, which become halides after consumption of their oxygen. This is only practical with barium chlorate, which was used until some time after World War I in the United States in military formulæ, but which according to Fedoroff is not used anymore. Strontium and barium perchlorate are much too hygroscopic for practical use.

A more practical approach is the use of the nitrates of barium and strontium as oxidizers, followed by their partial conversion into halides by combining them with the oxidizers potassium chlorate or perchlorate. The chlorate is eliminated for military purposes because of its hazardous behavior in combination with some fuels. Potassium perchlorate is best suited because of its stability, nonhygroscopicity, the negligible tinctorial effect of the potassium (as long as the quantity is not too large), and the capability of the residual chloride to react with the residue from the strontium or barium nitrate to yield the desirable alkaline earth chlorides. However, this secondary conversion can only be a partial one and is further limited by the fact that the amount of perchlorate must in many cases be small because of its accelerating influence on burning rate. It is therefore necessary to introduce a specific halogen donor of high chlorine content. The favorite materials are organic compounds: hexachlorobenzene, (C_6Cl_6) with 75% chlorine; polyvinyl chloride (PVC), with 64% chlorine; and the rarely used dimer of hexachlorocyclopentadiene, Dechlorane* ($C_{10}Cl_{12}$), with 78% chlorine. Apparently not used as color intensifiers in military work are Parlon,† a chlorinated polyisoprene rubber with 67% chlorine, and the common smoke ingredient, hexachloroethane (C_2Cl_6) with almost 90% chlorine. It should be noted that hexachlorobenzene (C_6Cl_6) is different from benzene hexachloride ($C_6H_6Cl_6$). The latter occurs in five isometric forms, one of which is a well-known insecticide (Gammexane, Lindane).

Copper powder or copper oxide is occasionally added to green formulæ as a flame color intensifier. The conventional binders are used sparingly in order to minimize weakening of the flame color by luminous (sooty) burning. This is especially important in flares of low luminosity where, incidentally, one must also consider that a cardboard tube may have undesirable burning characteristics. The luminosity of the flame is boosted by the addition of varying amounts of magnesium powder, which increases the visibility at greater distance or in daytime, but contributes nothing to the coloration; indeed it tends to overpower it.

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* Trademark of Hooker Chemical Company.

† Trademark of the former Hercules Powder Company.

Yellow flame presents no difficulty considering the very strong tinctorial power of the yellow sodium light. Because of its low hygroscopicity, the oxalate is nearly always used to introduce sodium. There would seem to be no reason to abstain from the use of highly purified sodium nitrate if the flare could be fully protected from the influx of high humidity during storage. It should be noted that according to Douda, halogens depress the color radiation for salts of alkali metals such as sodium[61]. Furthermore, a series of formulations involving mainly magnesium and sodium nitrate, with or without added sodium oxalate, point toward an improvement in color purity with the presence of the oxalate.

The most difficult color to produce in satisfactory depth is blue. This problem is less serious in the fireworks art, but the materials used there are viewed with suspicion in modern ordnance formulation. The essential color producing element is copper, which emits a blue light in the presence of chlorine.

Table 17-9 gives a fair cross section of recent developments in colored-flame formulation. The novice in the field must be baffled by the fact that white and colored flares are so closely related in composition considering the differences in generation of visible radiation of wide or narrow wavelength bands. The reason is that the formulation of colored light sources is a series of compromises between visibility and color recognition. A consequence of this similarity is that the techniques of mixing, pressing, and fusing are identical. However, in colored flares of low luminous intensity one must avoid the presence in or near the flame of objects that may be interfering light emitters, such as residues of some first fires, cardboard that contains luminous substances (principally sodium), or residues from fuse trains.

The instrumentation for measurement of colored light output is identical with that employed to measure white light. For chromaticity coördinates, and other data specifically pertaining to color, the photometric measurements must be modified by simultaneously employing several sensors, with or without a variety of filters which permits the passage of light in limited wavelength ranges.

Chapter 18

Delay Trains

Introduction and History

If a pyrotechnic mixture that is neither extremely violent nor too sluggish in its reaction is spread out in the form of an elongated powder train, or is tamped or compressed in a narrow column and ignited at one end, the reaction generally proceeds in an orderly fashion as shown by a glow or flame front. This may be followed visually beginning with prime ignition and through the final pyrotechnic event.

The history of pyrotechnic delay timing until about the year 1929 can be summarized in two words – black powder. This all-purpose material furnished not only propulsion, firework effects, and explosive force, but in proper arrangement and with modifications in composition, formed compressed powder columns or elongated fuse lines of the types still used in fireworks and some military devices. However, the modern requirements of extension of timing range, high stability, and complete confinement (obturation) led to a search for low-gas delay formulations. The earliest efforts starting around 1929, involved silicon and red lead (Pb_3O_4) or lead chromate ($PbCrO_4$). Glycerine was added, probably because it has binding power with lead oxide. These early mixtures were gas-forming to some extent. They were followed by truly low-gas mixtures, such as barium peroxide with the chalcogens, patented as early as 1934. Iron or antimony with potassium permanganate were tried and used in Germany, but never became popular in this country. World War II provided a new impetus to research and development of the "gasless" delay formulations and the work on improving them has continued ever since – not steadily but rather by sporadic efforts.

Delay Ranges and Uses

Pyrotechnic delay timing covers an approximate range of 0.06 to 250 cm/s. Since there are practical limits to the length as well as to the shortness of a powder column at which reproducible functioning can be achieved, time intervals available range from 5 milliseconds to 5 minutes. Where this range is insufficient, it can be extended to the microsecond range by using primary explosives, sometimes in combination with highly active pyrotechnic mixtures. In the long time-delay zone of minutes, hours, days, or weeks, certain chemical or physicochemical effects of corrosion (*e.g.*, by acids on metal) or of gradual softening (*e.g.*, by acetone on celluloid) can be utilized. These means for long delay times are not pyrochemical in nature, but they are treated in some detail since they are associated with incendiarism and explosive demolition.

Delay action below 1 msec and in the lower millisecond range is used in projectiles and bombs that explode upon impact with the target but which may do greater damage if a time delay is interposed in order to detonate the missile after penetration of the target.

In the millisecond range, from 25 to 1000 msec, the delay action provides for effective blasting in quarries, salt mines, and numerous other commercial applications of explosive charges. Staggering the explosions in a series of boreholes reduces vibration and improves fragmentation. It has special advantages in grade construction work.

The range 1 to 6 seconds is used in ground chemical munitions such as smoke pots, tear gas and smoke grenades, and fragmentation hand grenades, as well as in photoflash cartridges and similar air, or space-launched signals. With such items, it is imperative that the exploding or otherwise hazardous object is safely removed from the point of initial activation. Certain riot grenades allow 1.4 to 3 seconds delay action in an integral fuze that terminates in a detonator. The bouchon type detonating fuze M206A 1 is used in a white phosphorus smoke hand grenade with a delay of 4 to 5 seconds.

Longer delay times, up to 60 seconds, are found as part of so-called delay switches. Following an electric initiation, these devices undergo a pyrotechnic delay action that is followed by a mild explosive effect from a small charge of primary explosive. The latter causes a piston to move, opening or closing one or more electrical connections.

For some applications, sequential timing may well go beyond 60 seconds. It is possible to arrange delay trains of slow-burning mixtures to allow up to five minutes delay time, but for longer periods, the items become rather cumbersome. As previously stated, the slowest of the currently-used delays burns at a rate of 0.06 cm/s at atmospheric pressure, and considerably faster under confinement. Thus, about 25 cm of column length have to be accommodated in a 5-minute delay unit. This has been achieved by Ellern and Olander in an internally vented arrangement known under the trademark Pyroclok™ [70].

Devices for the longest delay timings are nonpyrotechnic. They are used as bomb fuzes and mainly constitute an harassment factor; paradoxically, the effect of the munitions as a deterrent is even greater the less reliably their timings operate, as they can remain hazardous even after the end of the hostilities! These somewhat unpredictable delays are used, for instance, by military forces in tactical retreat, to initiate concealed explosive or incendiary charges to function after withdrawal. The units that permit such delaying action for hours, days, weeks, and in extreme cases for months, will be described below. They are quite small and compact, while clockworks for longer time intervals become quite large and heavy and have other disadvantages, although they are indispensable when the required time interval must be accurate to minutes or seconds.

The events outlined for the various timing ranges are only a few examples out of a large number of delay timing sequences. There are many others such as the ignition of a fireworks display subassembly at or subsequent to the burst of a shell or rocket in the air, or the similar display of an emergency signal after being shot out of a special pistol. Parachute flares may use consecutive delay times for free fall, opening of the 'chute, and ignition of the flare candle. A few gun-projectile fuzes employ powder trains rather than mechanical timers.

We shall see later that all chemical delaying devices (pyrotechnic or otherwise) have large temperature coefficients and only fair accuracy at any one temperature. The reason for their use is economic and tactical, since no explosive component parts or assembly jobs are involved and millions of delay columns can be produced by relatively unskilled labor on easily set up assembly lines. In addition, such small, highly compact and heavily enclosed devices are rugged, stable, and have no moving parts that might need servicing after prolonged storage. In short as well as long delay timing, the added advantage of smallness is a factor, though in the minute range, clockworks may be lighter and more compact. Then, however, the problem of initiation of clock action has to be considered.

Factors in Formulation and Design

In discussing the field of delay timing by pyrochemical means, the first question to arise might be the calculation of the burning time (rate) from the reaction of the components and their chemical and physical properties. Burning time depends on the following factors, enumerated roughly in order of significance:

1. Nature of the reactants and products;
2. Particle sizes (especially of fuels);
3. Relative amounts of ingredients (especially of metal fuels);
4. Ambient pressure;
5. Ambient temperature;
6. Compaction;
7. Diameter of column;
8. Nature of envelope (casing).

Without undertaking detailed analyses of this seemingly inexhaustible subject, a few random notes will be added on the various parameters of delay performance.

One of the slowest mixtures (though not one likely to be used as a delay formula) consists of 96% ammonium nitrate and 4% charcoal, with a burning rate of 0.008 cm/s at a density of 0.94 g/cm^3. This corresponds in burning rate to the article called "slow match," a type of string fuse that consists of loosely twisted cotton cord steeped in a solution of saltpeter and sometimes lime-water. Rope or wick-like extremely slow smoldering fuses made of cellulose fibers and perhaps very lightly impregnated with a nitrate* are occasionally used in clandestine work, but they require some ambient air. A study on the burning of cellulose may be of significance in this context: the impregnation of alpha-cellulose paper with 1.5% of potassium bicarbonate ($KHCO_3$) completely suppresses flaming, but it increases the sensitivity to glowing ignition and presumably enhances continued burning.

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* The use of lead nitrate is endorsed in some early works on fireworks[126], and could be applied to military as well as recreative pyrotechnics.

Another allied topic is the relation of the burning rate and temperature of tobacco leaf to its potassium salt or chloride content. The burning temperatures are roughly inversely proportional to the potassium content. The glow time of a tobacco leaf is more than twice as long at the tip than at the base. Cigarettes have been used as delay fuses in firesetting since they do not go out; with some precautions as to support and positioning, the rate of glow progression for American cigarettes is on the order of 0.4 cm/min in still air.

The slowest delay mixtures that function properly under a great variety of conditions are those based on very finely powdered and chemically active metals of highest density, especially tungsten.

At the other end of the timing scale, considering the influence of specific materials on delay time, are mixtures containing zirconium of subsieve fineness. The previously described first fire mixtures have a burning rate of 25 cm/s. Still faster are mixtures of an excess of the finest molybdenum powder combined with potassium perchlorate.

Because of the limitations of choice of oxidizers in delay mixtures, especially of the low-gas variety, data on changes in burning rate with change of oxidizer are scarce. Red phosphorus has been paired with a number of oxides and chromates and not surprisingly, the relatively most active oxidizers such as silver oxide (Ag_2O) and barium peroxide (BaO_2) produce very fast compositions, while highly stable oxidizers such as barium chromate ($BaCrO_4$) and the oxides of iron yield very much slower burning rates, and cuprous oxide (Cu_2O) stands in between.

In the intermediate pyrotechnic timing range of about 0.25 to 5 cm/s, modern practice employs a variety of metal powders, and other elements that behave like metals, such as silicon, boron, selenium, and tellurium. These must be pyrochemically quite active for reliable fire transfer, but not so active as to yield only very short reaction times. They may be used with two oxidizers, one of them often being the rather inert barium chromate, while the other is much more reactive and heat-forming, such as potassium perchlorate. This system permits a wide variety of formula changes and therefore of burning times, though the type and amount of fuel is generally the overriding factor. Suitable fuels have been found by trial and error: besides silicon and boron, the most popular are certain alloys of zirconium and nickel, and the metals manganese, tungsten, molybdenum, and chromium. All the delay formulæ, no matter how seemingly well standardized regarding specific properties of ingredients, mixing, and pressing procedures, are capricious and a constant source of difficulties to the manufacturers – sometimes more so than the main item which the delay mixture ignites. The so-called D16 series, with a range of about 3 to 13 s/in, using manganese, barium chromate, and lead chromate, seems to give less trouble than the others.

In German World War II ordnance, combinations of antimony metal and potassium permanganate were favorites.

In the United Kingdom, work on slow-burning mixtures has continued to follow the trend of employing high-gas mixtures using such fuels as tetranitrooxanilide or tetranitrocarbazole with barium nitrate.

C.H. Miller[168] showed that the burning rate of $B/BaCrO_4$ varies with pressure only when then mixture is prepared mechanically, but not when the mixture is co-precipitated. This may indicate a general method for preparing pressure-insensitive delays. McLain[161] cites unpublished data on the lead oxide/silicon system over a 100 atm pressure range and finds these to achieve a plateau in burning rates above 20 atmospheres. McLain also cites the various mixtures used for delay detonators which assure precise delays in blasting operations. These delays must be sealed to assure reproducibility in timing. Manufacturers make two series of delay detonators, one with half-second increments, range from 0.5 to 5s, and the other in 25 to 35 ms increments, designated by numbers 1 through 10. Millisecond delays typically contain lead oxide/silicon (propagation velocity approximately 4 cm/s). Half-second series contain 64:36 $KMnO_4/Sb$ and one-second delays 70:30 $KMnO_4/Sb$ (propagation velocity approximately 0.2 cm/s). These and many new mixtures are characterized by the absence of chromates. Further examples are Zr/MoO_3, 2.5-16 cm/s (U.S. Patent 3,703,144) and $Sb/FeO/KClO_4$ 35:43:22, for 0.5 second caps (Ger. Offen. 2,416,920).

The propagation rate of Mg/Teflon mixtures was studied[134] and it was found that the rate increases when the proportion of magnesium is above stoichiometric (33%). As the amount of magnesium vapor burning in the gas phase above the mixture increases, the heat flux increases and so does the burning rate.

Particle size of the metal fuels in delay mixtures is of great influence. It is often necessary, in order to match an existing composition, to proceed by trial and error using samples of various production batches of the metal fuel. One may find in some cases, in particular with tungsten, that the pyrochemical behavior of metal powders may vary enormously even when particle sizes seem to be little at variance. On the other hand, the grain size of an active oxidizer such as potassium perchlorate has little effect on the burning rate, though it may influence ignitability.

The percentage of metal fuel in a formula has a decisive influence on burning time, usually insofar as burning times become faster and faster with excess of metal. This appears to be a function of the increased heat conductivity of the mixture rather than of the increased surface area of the active fuel, since the admixture of silver powder in lieu of part of the excess fuel has been observed not to alter the burning rate. It is certainly remarkable that whatever the mechanism of action is, high metal powder content surpasses the caloric output as a factor in the burning rate, sometimes until 95% metal powder is present.

Regarding the percentage of oxidizer, if two competing compounds, such as potassium perchlorate and barium chromate, are present, it is important that the metal be in stoichiometric excess in relation to the more reactive oxidizer, in this case the perchlorate. This is the case at least in obturated fuzes, since indications are that free oxygen is otherwise released. Beyond this condition, it seems to have little effect on burning rate whether, *e.g.*, 5% or 10% perchlorate is present.

Even though the greatest effects of gas pressure on burning time are found where high pressurization is encountered, as in completely enclosed systems, the rarefaction of the atmosphere due to variations of altitude must be considered for open-burning fuse trains. Safety fuse (see below) with a burning rate of 0.8 cm/s at or near sea level will be 5% slower at 1700 m. Extreme conditions would be encountered on high-flying airplanes or on missiles but delay columns for proper functioning in these cases are designed to be independent of external pressures. Such enclosed systems do not react, however, at the same burning rate as open ones since no "gasless" mixture is free from developing a certain amount of volatile and pressurizing substances, as previously explained. In addition, self-heating during the reaction, interstitial air contributing to pressurization with rising temperature, and the gaseous products of primer fire all have a share in speeding up the chemical reaction of the column.

Theoretically it might be possible to design sufficient internal vent space to annul the influence of such pressurization and also to provide a large "heat sink," but this is hardly practical. A compromise is possible, however, and is now often employed.

If the confinement of low-gas mixtures includes only a minimal "vent" volume, the burning rate of the column is considerably increased as burning proceeds. In one case where a very slow-burning tungsten mixture was thus employed, the burning rate was doubled. Even the better internally-vented devices are rarely provided with adequate vent volume to approach open burning conditions, and the burning rate is increased the smaller the allotted vent volume.

The temperature coefficients of low-gas delay columns have been studied quite extensively. Within the most often tested interval, −50° to +70° C, a temperature coefficient of 0.14%/°C is a reasonable figure. This means that the variability of delay time over the indicated range of 120° C would amount to ±9% attributable to temperature change only. Exceptionally, the range may be less, but often it is much higher. Crowded design, because of size limitations, often provides inadequate vent space, causing a failure to dissipate heat that in turn leads to excessive pressure build-up. Considering variability due to uncontrollable aspects of manufacture and of burning behavior itself, a burning-time range approaching ±20% may have to be allowed.

Significant design features of the delay column and its envelope comprise the degree of compaction of the mixture, the diameter of the delay column, the thickness of the tube or block into which the powder is pressed, and the material from which the enveloping support is made. The burning time and, in some respects, the reliability of the item itself vary with these factors; increased compaction means slower reaction speed, the variation being considerable at first, but when a certain degree of compaction has been reached, an increase in pressure changes neither density nor burning rate very much. In other words, the compaction pressure *vs.* burning time can be represented by a curve steeply ascending and then asymptotically tapering off, the turning point for the more common delay compositions being at 2200 to 4000 kg/cm^2.

The diameter of the delay column may become critical when the composition is slow-burning and the heat output is small, as is often the case. A column diameter of 0.50 cm is usually adequate and if the ambient temperature is never expected to be very low, successful burning is possible at 0.28 cm diameter. Otherwise, a composition may perform adequately at normal and at higher temperatures but at extremely low temperatures enough heat may be dissipated in the surrounding metal that the glow front becomes narrower and literally "tapers off;" burning may cease before the terminal fire transfer is achieved. By the same token, decrease in the tube wall thickness will tend to concentrate the heat in the column (that is, it will dissipate less heat per unit of time). The result may be a faster burning rate with decrease of wall thickness. Studies on the influence of the nature of the container – *i.e.*, of its heat conductivity – have been less conclusive, but undoubtedly the selection of ceramic bodies as compared to metallic would have a favorable influence in marginal situations and especially where multiple columns occur in close proximity.

The effect on burning rate of thermal losses through the walls of delay columns was examined by this author[100] and found to be rather small. Most delay column mixtures have a very low thermal conductance, the dependence of which on temperature is known to be small.

One effect of heat conductivity along the column wall may be premature initiation of whatever terminal charge follows the delay column. This "anticipatory effect" has been attributed by Picatinny Arsenal researchers to permeation of the unburned column by hot gases. Whatever the actual reason, some possibility exists that the terminal effect by which the delay time is measured is not caused by the glow front of the column actually reaching its end. In some unhappy circumstances, the delay column may be bypassed in its entirety. In reverse loading situations, where a sensitive first fire is pressed first and some of it is retained along the tube wall during subsequent filling of the tube with delay mixture, this may contribute to premature fire transfer. Mechanical breaking up of the column has the same result. There is, of course, hardly a more unfortunate effect than instantaneous action in lieu of delayed action because it may cause the user's death, as in the case of hand grenades.

As can readily be seen, the actual design and assembly of delays where high reproducibility is required, involve numerous technical skills, and even then, unexpected deviations from proper behavior may baffle the pyrotechnist. Highly polished internal surfaces, use of dead-load presses or other means of precise pressure control, automatically preset advance and dwell times of the pressing ram, pressing in small increments, perfect leak-proof sealing of the unit, and use of the most uniform prime ignition sources are some of the conditions that will improve pyrochemical delays.

Commercial Fuse Lines

Ignition lines and tubular fuse trains can be used for delay timing in fireworks items and in some military signals, but in general do not burn consistently enough and are not physically suited to withstand the rigors of military surveillance tests and actual exposure in use.

Safety fuse is described as a tightly wrapped train of potassium nitrate black powder having approximately 1 cm/s burning rate with a normal variability of ±10%. The coating of such a fuse is most often an impregnated textile with more and more effort being made to improve the moisture-sealing effect by use of a coating or a plastic tubing, as in polyethylene-covered safety fuse.

Quickmatch consists of cotton strands impregnated with black powder mixed with starch paste or dextrin. "Mealed" (Class A, or dusted) quickmatch contains additional fine black powder as a coating which increases the rate of burning. The specified burning times lie between 1.8 and 3.8 cm/s. When the rather rigid and brittle pieces of quickmatch are bent, threaded through holes, and thus partially broken up, the burning rate increases considerably, hence quickmatch is more suitable for fire transfer as such rather than for timing. In fireworks use, quickmatch is often "piped" (enclosed in a light paper tube), rendering it nearly instantaneous. The fabrication of delay columns in "endless" lines and cutting these to size, rather than resorting to the tedious individual production of single items, seems enticing. If soft lead tubes of 1 cm internal diameter and 2 cm outside diameter are filled with delay composition, closed on both ends, and swaged to a 1/4 inch outside diameter, a compacted delay fuse line results, which can be cut in short lengths or bent and formed into a spiral if desired. The development of this type of delay has been pursued in the United Kingdom, while in this country similar processes have been employed for explosive line charges. Considering that a delay unit must be provided with ignition and terminal fire transfer material and fitted in a larger assembly of some kind, it seems doubtful that this type of fuse train is of much use except under the same conditions where existing safety fuses are useful. One exception is the insertion of delay trains into detonators. Mixtures of barium peroxide and selenium, or slower ones with tellurium have been tamped into lead tubes and consolidated by swaging, starting from three feet length and ending up with four feet of fuse, a process used by the Hercules Powder Company for over thirty years.

Nonpyrotechnic Long Delays

Since there is a limit to the length of any fuse train, the use of pyrotechnic means must yield to other progressive action for long duration. Clockworks for periods of days and weeks are even more cumbersome and expensive than for short duration, but chemical action or the swelling and dissolving action of a liquid on a solid are simple means for long delay timing.

The M1 Delay Firing Device, MIL-F-13893B (Ord) (1962), commonly called the delay pencil, is a World War II invention of the Allies but was captured by the Germans and used by both sides. It is based on the corrosion of a tinned steel wire by solutions of cupric chloride in water/glycerine mixtures. The wire is held under 8 kg spring tension and its corrosion and eventual breaking releases a firing pin acting either on a percussion primer (M27) or on a miniature incendiary containing the tip of a strike-anywhere match as described in Chapter 11. Because the glass ampoule with the corrosive liquid is an integral part of the device, each delay time requires a separate pencil. Each kind is marked by a lacquered metal band of a different color, which also serves as a safety detent.

The pencils are made for delays calibrated in minutes as well as hours, assuming an ambient temperature of about 20° C. The temperature coefficients are very high and increase with the length of the nominal delay time. The device is used for incendiary or demolition purposes in clandestine activities. Two pencils attached to one item increase reliability of firing and reduce the probability of a "delayed delay action" or of failure due to a hung-up firing pin, which occasionally occurs. A hazard of the device is corrosion of the wire in storage, be it because of breakage of an ampoule or through external influences. While a peephole allows a check on a fired but retained striker, it is not possible to discern whether a partial corrosion has left the device at the brink of firing.

A different principle is involved in fuzes, of which the Long Delay Tail Fuzes ANM123 are examples. The delay action is initiated by the softening action of solvent on a celluloid collar that retains a firing pin. Vials containing solvents of varying activity toward nitrocellulose (acetone being the most active, esters least) allow a nominal delay range of 1 to 144 hours. Again, the temperature coefficient is high – for up to 12 hours nominal delay, a timing ratio varying from 1:9 to 1:24 applies within the relatively small temperature range of −10°C to +110° C. The slow-acting solvents become quite unreliable at low temperatures because they may not dissolve but only swell the disk, which then may remain strong enough to hold back the striker. As a result, this type of fuze may stay suspended for many months or years, and either never go off, or go off only after unpredictable gradual shear.

We have seen earlier that pyrochemical action between sulfuric acid and chlorate mixtures can be used in combined delaying and ignition devices. This can be done by making use of the corrosive or hygroscopic actions of the acid, or the active components can be brought together by tilting or spilling, an effect that may be produced from some gradual, external process of a simple nature.

Composition of Delay Mixtures

Pyrotechnic delay mixtures are usually classified as 'gasless' and they burn (in theory) at rates independent of ambient pressure. As is usual with generalizations, there are limitations to this rule that require some elaboration. Burning rates of delays depend on a number of factors such as heat output, particle size, stoichiometry, ambient pressure, temperature, compaction density, thermal conductance and whether the mixtures are confined (obturated) or not (vented). Tungsten and manganese delays have been found to be the least variable and therefore will be the focus of attention.

Burning rates are expressed either as lengths per unit time or as 'burning time,' the inverse of burning rate. In this book the burning rate is the preferred expression, as it is desired to discourage the practice of citing burning times in seconds without specifying the unit of length. In some laboratories the convention is the

Table 18-1. Typical Delay Variability[242]

	Burning Rate cm/sec	% Variation at 22° C	% Change in Burning Rate from -54° to +22° C
Tungsten Delays	0.07 - 0.08	1.5 - 3	10 - 11
	0.10 - 0.13	2 - 3	8 - 9.5
	0.51 - 0.85	2 - 5	5 - 6
Manganese Delays	0.85 - 1.30	1.2 - 2.5	5 - 8
	0.36 - 0.85	1.2 - 2.5	5 - 13
	0.21 - 0.28	1.2 - 2.5	10 - 15

other way. Various delay mixtures were examined critically by several authors[109, 148, 198, 209] and their data form the basis of this discussion.

Tungsten delays are composed of tungsten metal, barium chromate, potassium perchlorate and diatomaceous earth (see Table 18-2). Usually the burning rate of pyrotechnic mixtures increases with heat output, but with tungsten delays the opposite is observed, because the rate is determined by the thermal conductivity of the mixture. Therefore, as the percentage of tungsten increases, thermal conductivity and burning rate also increase. The burning rate decreases with the addition of calcium fluoride (which acts as a diluent) but increases with the percentage of diatomaceous earth (silicon dioxide). Silica lowers the decomposition temperature of barium peroxide and, presumably, of barium chromate.

Many delay mixtures, including the tungsten delays, function in smaller time intervals than might be predicted from propagation rate data, when in contact with thermally sensitive charges (*e.g.*, primary explosives). This time reduction is called the "anticipatory effect." For tungsten delays it is equivalent to 0.2 cm of the column length[169]. This effect can vary quite substantially as shown in Figure 18-1.

The change of burning rate with temperature (the temperature coefficient) for tungsten delays is about 0.03%/°K[199] when tested in vented units, but marked deterioration was found when the same units were exposed to a highly humid atmosphere. Tungsten delays are not, strictly speaking, gasless, because on combustion an appreciable atmosphere of volatile tungstic oxides and volatile tungsten and chromium oxychlorides is formed.

Manganese delay mixtures date from World War II. Aging of these delays (bringing about a reduction in burning rate of about 0.007 seconds per centimeter per year) is ascribed to the corrosive effect of moisture on the metallic fuel. To inhibit this deterioration, the manganese powder is treated first in a potassium dichromate bath, then by a protective coating of stearin. The stability of the mixture increases with decreasing particle size of the manganese. Stability is highest for fast-burning compositions having a large fraction of lead chromate. Pretreatment of the manganese is unnecessary for delay mixtures that will be kept dry[199].

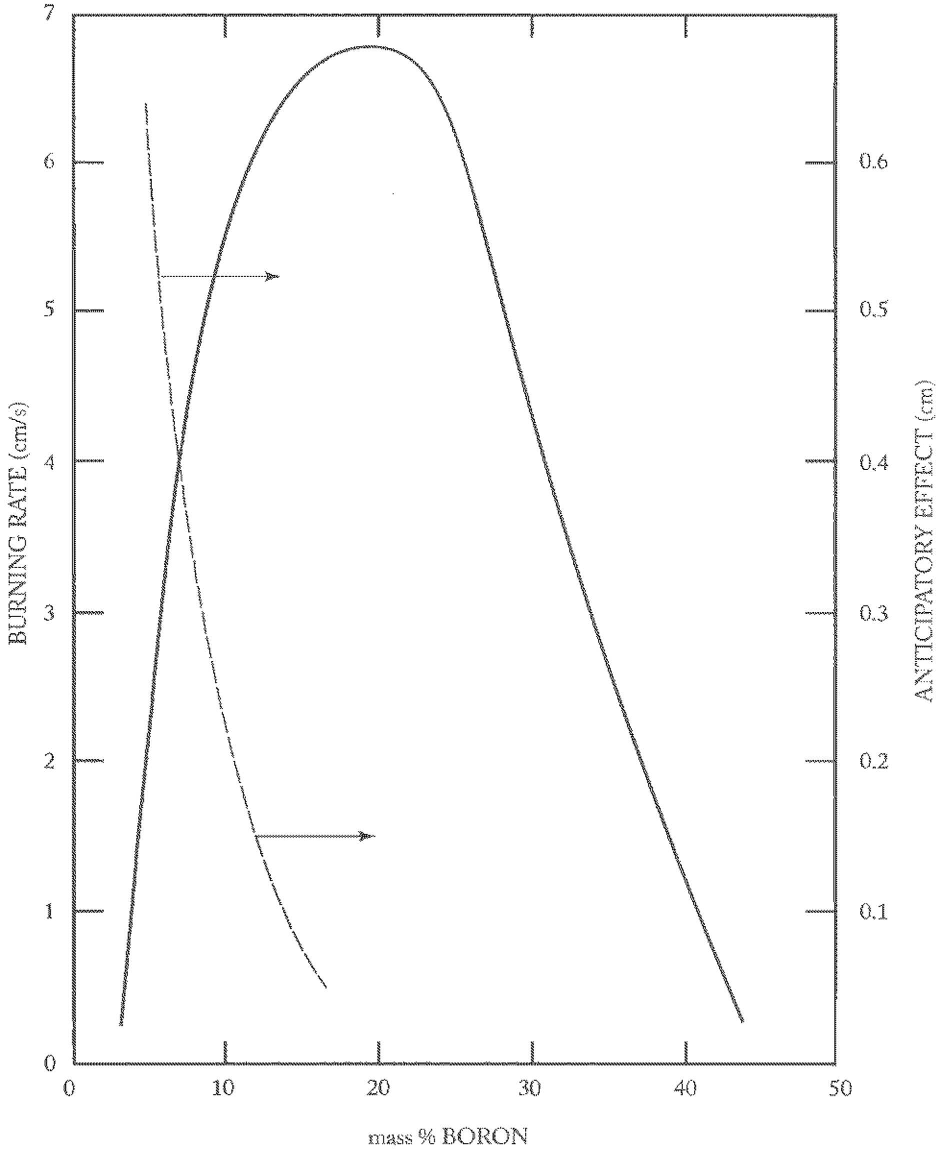

Figure 18-1. Burning characteristics of boron/barium chromate delay compositions[169].

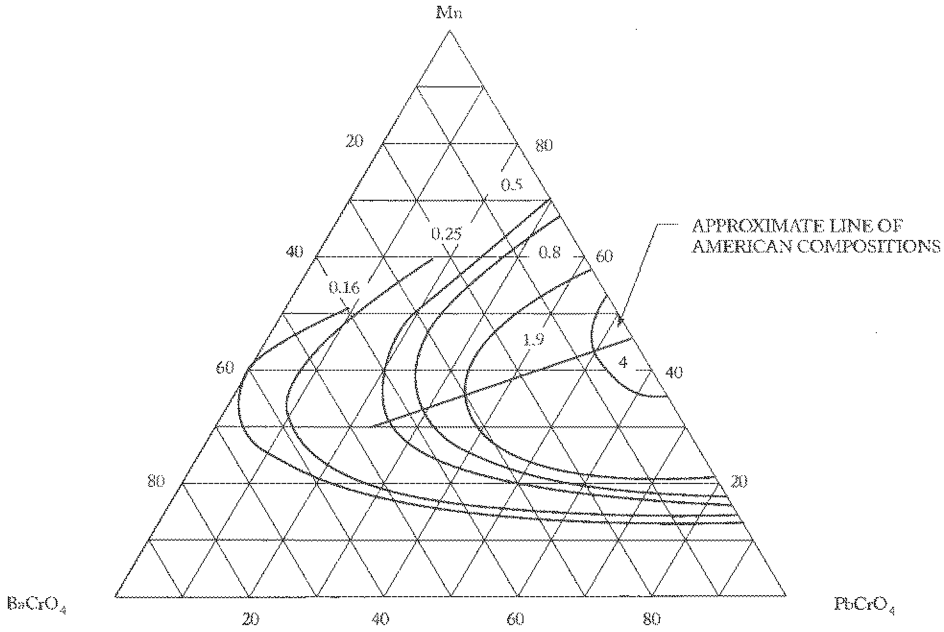

Figure 18-2. Burning rate contours of manganese delay compositions, cm/s.[252]

Manganese delays burning more slowly than 0.18 cm/s do not ignite reliably at low temperatures[252].

In books on pyrotechnics formulæ have traditionally been listed for all types of mixtures, often to four significant figures, even including trace components which may have no function other than to color or lubricate the mixture. Doubtless such minutiæ are important, but do little to give insight into possibilities for substitution or of the potential for changes in performance. This is illustrated in Figure 18-2. For ternary mixtures, such triangular graphs are particularly convenient[131].

The traditional delay compositions all contain chromates in some combination, for reasons that were explored in the discussion of alkaline earth chromates in Chapter 16. As noted in Chapter 3, hexavalent chromium is suspected as a carcinogen and some effort has been devoted to finding a replacement[53]. It appears that mixtures of metal powders (W, Ti, Mn, B) with permanganates, manganese dioxide and potassium perchlorate may meet the range of propagation rates now obtained with chromates. Silica, added to potassium perchlorate, increases the rate significantly, a phenomenon encountered earlier with barium peroxide. In the United Kingdom, boron/bismuth trioxide delay compositions have long been employed, being gasless and having burning rates of 0.5 to 3.5 cm/s.[43] Their moisture sensitivity requires careful sealing if changes in burning rate over a lapse of time are to be avoided.

Table 18-2. Survey of Delay Mixtures[129]

	1	2	3	4	5
Potassium perchlorate	–	–	14	10	10
Manganese	29	–	–	–	–
Lead chromate	26	–	–	–	–
Barium chromate	45	85-97	60	55	55
Boron	–	3-15	–	–	–
Zirconium/nickel alloy	–	–	26	–	–
Viton (a fluorinated rubber)	–	–	–	1	–
Tungsten	–	–	–	30	30
Silicon dioxide	–	–	–	4	5

Burning Rate, range, cm/s: 1) 0.18 - 1.25 (obturated)
2) 3.1 - 4.3 (obturated)
3) 1.25 for 70/30 Zr/Ni
0.21 for 30/70 Zr/Ni
0.13 with up to 10% CeO_2 added (vented)
4) 0.16 - 0.25 (vented)
5) 0.06 - 0.25 (vented)
0.04 with CaF_2 added

Chapter 19
Incendiaries and Tracer Munitions

Incendiaries

Tracer bullets originated during World War I when they also served an incendiary function. Except when filled with white phosphorus and used against hydrogen-filled balloons, these bullets were found to be quite ineffective. Moreover, the early formulations were unreliable in ignition and had a short storage life. The history of the development of small arms incendiary munitions was reviewed in a lengthy, four-volume report by the Denver Research Institute[42].

Present-day small arms incendiary munitions are limited to starting fires in helicopters. Larger caliber incendiary rounds, particularly those having armor piercing characteristics, are used against ground transport and armored personnel vehicles. Incendiary rounds up to 20mm caliber are initiated by impact, while larger caliber projectiles are fuzed. The interested reader is directed to the specialized literature such as the *Encyclopedia of Explosives*[72] or Caven's and Stevenson's report[32]. Typically these contained magnalium, titanium, or zirconium powder with potassium perchlorate.

Incendiary ammunition and bombs contain pyrophoric metal components when intended for use against flammable targets such as fuel depots. Because it is usually difficult to ignite structural targets with devices having a short burning duration, incendiary bombs for deployment against flammable structures rely either on Napalm (strictly speaking, not a pyrotechnic formulation) or on thermitic reactions. Military thermites are composed of granular aluminum and coarse iron oxide scale, and are made more easily ignitable by the admixture of a small amount of barium nitrate. This mixture was used in the familiar hexagonal shaped 2 kg magnesium alloy bomb which was extensively dropped on European cities during World War II.

Incendiary action is connected in a complex way to the interaction between projectile and target, and the interaction between the incendiary and the combustible. The total heat input must be sufficient to raise the combustible to the ignition temperature, and then, sufficient oxygen must be available to support combustion. The question as to whether the heat input is sufficient can be answered analytically by a numerical solution of Fourier's Equation with a source term:

$$\frac{dT}{dt} = \propto \nabla T \qquad [19\text{-}1]$$

where: $\propto$ is the thermal diffusivity $\left(\frac{\kappa}{\rho C_\rho}\right)$
κ is the thermal conductance
C_ρ is the heat capacity
ρ is the density
h_c is the heat of combustion
T is the Temperature
t is the time

As a first approximation, the length of time an incendiary at a temperature above the ignition point of the combustible must be in contact with the combustible is proportional to $L^{2/\propto}$ where L is the nominal size of the combustible. Solutions of the above equation can be performed with a great deal of elegance, but in practice incendiary munitions are tested on simulated ("replica") targets[42] or in "arenas," namely against an array of combustibles.

The problem of igniting combustible vapors (as in aircraft or fuel depots) is more complex than that of igniting solids. Liquid fuels must be dispersed (or evaporated) so their concentrations in air will be within flammable ranges. Much effort has been directed toward developing incendiary munitions with a one-shot ignition capability, but with the increasing speed and altitude of aircraft, lowered vapor pressure of fuels, and development of self-sealing aviation fuel tanks, this goal has proven to be an elusive one.

In recent years, zirconium sponge has emerged as one of the principal constituents of incendiary hardware, having displaced magnesium in this application. This has been demonstrated in the Air Force programs for development of the BLU-61 and the BLU-85 configurations.

The World War II development of stable gels from liquid fuels for use in flame throwers and incendiary bombs was mainly the work of scientists at the Chemical Warfare Services Laboratory at Massachusetts Institute of Technology. The most satisfactory of these was Napalm, the name derived from its main ingredients – aluminum NAphthenate and PALMitate. Concurrently with these efforts at the start of Word War II, Standard Oil Development Company worked on a sodium soap thickener. The most recent developments omit the soaps altogether and use a large amount of synthetic plastic compound. The mixture, called Napalm B, while solidifying at 35° C, will remain a viscous liquid even on exposure to lower temperatures.

Congealing a liquid fuel has the advantage in incendiary practice that the burning gel does not run even if unsupported, *e.g.*, if splattered from a bomb or after a casing burns away. Thus consumption is slowed down and the flame remains localized. With flames of relatively low temperature (where heat transfer is chiefly convective and conductive) duration is of the greatest importance for ignition of heavier wooden structures. Thus, Napalm – a term now popularly understood as the congealed liquid rather than the thickener – is one of the most effective incendiary agents.

Sterno® is a well-known commercial gelled liquid fuel. It burns with a nearly invisible flame and little residue, and these properties, as well as its odor, proclaim it to be mainly alcohol. It is a handy heat source for campers, hunters, and explorers. According to a U.S. patent (US 2,721,120) it consists of an alcoholic solution of nitrocellulose, solidified by addition of a miscible non-solvent for the nitrocellulose. The latter is thus thrown out of solution and forms a voluminous mass that traps most of the liquid portion.

Since the appearance of pyrogenic, extremely fine silica (0.015-0.020 μm particle size), commercially known as Cab-O-Sil and by other tradenames, it has been possible to gel many liquids instantaneously by addition of several percent of the powder. A stable, firm incendiary gel can be made from Stoddard solvent with 8% of Cab-O-Sil.

A relatively cool-burning incendiary is white phosphorus. Some of its igniting and incendiary properties have been discussed in Chapter 16. Phosphorus by itself is an incendiary of limited usefulness, effective only against easily ignited objects.

Notwithstanding its deficiencies as an incendiary, phosphorus has a certain tactical value because of the power of obscuration caused by the volatility of its final combustion product, phosphorus pentoxide (P_2O_5), the spontaneous reignitability of doused, unburned residues and the severity of the wounds caused by burning phosphorus when it comes in contact with human skin. Its burning properties can be improved by mixing it with synthetic (GRS) rubber.

The magnesium incendiary bombs of World War II consisted of an alloy of magnesium with small percentages of aluminum, zinc and manganese. The use of such magnesium alloys goes back to World War I, when an alloy called "Elektron" containing 13% aluminum and some copper was developed. These additions increased the mechanical strength of the magnesium without affecting its ignitability. Sometimes, a much larger percentage of aluminum is mentioned, but such mixtures – the 50:50 alloy for instance – are very brittle, and more useful for conversion into fuel powder.

The filler for magnesium bombs such as the 2-lb. AN-M52A1 and the 4-lb. AN-M50A2 is a modified thermite called thermate-TH3, containing 25% Al, 44% Fe_3O_4, 29% $Ba(NO_3)_2$, and 2% sulfur. A similar mixture with synthetic resin binder is called TH4. TH3 thermate is also the filler in the AN-M14 Incendiary Hand Grenade. Even though by design this is a grenade for throwing, its main function is as an equipment-destroying item that might work more effectively if carefully emplaced.

The small hexagonal magnesium bombs were dropped in clusters, and since they are fairly easily rendered harmless by covering with dry sand, an explosive charge with variously delayed action was inserted into the weighted base to discourage firefighting. As an incendiary such a modified device becomes much less effective because the burning thermite is scattered. Because the bombs containing the explosive had a colored marking at the base, even the intent to inhibit counter-measures was in part defeated.

Thermite itself (25% Al, 75% Fe_3O_4) causes an extremely high heat concentration and is able to penetrate metal by means of one of its two reaction products, molten iron. Steel plates two centimeters thick can be perforated by a properly directed stream of the white-hot mass. While thermite can act as an incendiary because of its combination of convective or conductive and radiative heat, it is more valuable because of these penetrating properties, such as for demolition of machinery. Small amounts are too easily quenched to exert the proper persistent heat flow necessary for ignition of combustible structures. Because thermite is difficult to ignite, nickel may be added (as in Pyronol[110]) which promotes the thermite reaction through the nickel-aluminum intermetallic reaction. Likewise, the addition of barium nitrate and sulfur (see above) in Thermate TH4 serves the same purpose by lowering the ignition temperature. Ellern[70] mentions a thermite ignition mixture containing barium peroxide.

Thermite is most efficient in its typical manifestations when used without a binder. Because of a cooling effect, binders make ignition more difficult and cause heat flow away from the substratum. Counteracting this by the addition of a stronger oxidizer can partially remedy these faults, but if too much is used, the character of the thermite reaction is lost.

Plain thermite, TH1, in a relatively substantial amount is the ingredient in cryptographic-equipment-destroying incendiary units. Their purpose is the complete breakdown of electronic equipment by melting, burning, and severing of connections of certain classified devices. This task is not as easy as it appears, especially on a small scale and when the heat has to be contained, *e.g.*, under indoor conditions. Where the destruction can be performed by combustion, as with security-sensitive information written on paper, celluloid boxes containing sodium nitrate are successful, when interspersed between the documents in heavy filing cabinets, as the cabinet confines the conflagration.

Larger quantities of documents can be speedily destroyed by mixing them in an open pit, drum, or the like with about 140% of their weight of sodium nitrate. The destruction of the paper and also of admixed plastic items is very thorough, and any more resistant combustibles are likely to be gradually consumed in the large molten residue after the main reaction is complete. Any substantial admixture of combustible metals such as magnesium or aluminum must be avoided, since a disastrous explosion may occur.

Alkali chlorates can be used in the same manner and are valuable when the destruction is on a small scale and where the reaction of the paper, etc. with a nitrate might be too sluggish. However, chlorates do not form a substantial molten residue, because the alkali chloride is partly carried off by the smoke. Admixture of some nitrates may correct this deficiency, and perchlorate may also be added to increase oxygen supply.

A few remarks should be added about testing the effectiveness of incendiaries. It is quite appropriate to compare small incendiary units with the help of standardized wooden structures of moderate dimensions. They imitate actual conditions by creating some updraft between vertical parallel boards or by addition of horizontal and vertical members of wood of standardized size, composition, and moisture content. Similarly, the incendiary may be applied to other material and the progression of the fire transfer observed. Miniaturization is likely to give a false picture of the actual effectiveness.

Tracer Munitions

The function of tracer munitions has returned to their original tasks of fire control, range estimation and marking of target impact, *i.e.*, spotting. Again, the reader is directed to the technical literature for information on fire control by spotting[32]. The principal ingredient in spotting munitions is red phosphorus (with barium nitrate as an oxidizer) so that the characteristic white puff of smoke will serve as a daytime signature. Partial substitution of the phosphorus with zirconium produces a significant flash with day and night visibility. Hence, tracer bullets serve a number of functions. They also help to identify nighttime combatants (owing to their pronounced side visibility), to guide the direction of fire (fire control), to estimate range, and, by acting as a delay element, to self-destruct munitions[56].

Historically, storability, ignitability and burning time have been recurring problems in tracer munition fabrication. The endothermic decomposition of metal salt oxidizers and the brief exposure to the propellant flame (0.5 to 2 ms) brought about the need for special igniters and subigniters as shown in Table 19-1. Furthermore, the desire to hide the position of the gun at night by delaying tracer ignition for a short distance from the muzzle, required the development of so-called dim igniters.[57, 76, 186] The mechanism of tracer reactions is a complex one, as the burning rate and the brightness of the trace increase with the spin rate of the bullet[32] but decrease with altitude. The reaction equilibria were examined[103] and it was found that the solid phase is principally magnesium oxide.

One interesting development was a rocket assisted bullet which would theoretically have the advantage of a flatter trajectory, less recoil, and high impact velocity. Such small arms rockets have been proposed as anti-personnel weapons[74] but are currently not in use.

Smoke tracers which leave a colored smoke trail are used by aircraft gunners as practice rounds, the typical trace length being about 600 m. The compositions contain about 70% strontium peroxide and 10% each of calcium resinate and catechol, the remainder being methylaminoanthraquinone in red smoke trails and auramine for greenish-yellow smoke trails. In recent years, the carcinogenic nature of the dyes has prompted extensive work on the recovery and disposal of pyrotechnic smokes and tracers[180].

Several distinct pyrotechnic compositions are used in combination within the tracer munition. These are discussed in Table 19-1. The delay action igniter, I-136, is designed to hide the exact position of the gun at night by providing invisible burning in the bullet cavity for the first 25 to 200 meters. The composition contains no metal; the calcium resinate acts both as fuel and binder, also serving as a water repellent. The dim igniter, I-194, provides a slight visibility for the gunner at night, whereas the sub-igniter, I-280, enhances this visibility for daylight use.

Table 19-1. Igniter and Tracer Compositions[32]

Component	Delay Action Igniter, I-136	Dim Igniter I-194	Sub-Igniter I-280	Red Tracer R-284
Strontium peroxide	90	-	-	-
Magnesium	-	6	15	28
I-136 Igniter	-	94	85	-
Calcium resinate	10	-	-	-
Strontium nitrate	-	-	-	55
Polyvinyl chloride	-	-	-	17

A type of tracer was recently described[196] which is a variant of an infrared decoy. It consists of a tantalum-sheathed coil containing a Si/Pb_3O_4 mixture, which, located in the aft end of a surface-to-surface, wire-guided, anti-tank missile, serves to provide the bright image necessary for tracking.

Chapter 20
Generation of Smoke

Screening Smoke

The pyrotechnic generation of smoke is almost exclusively a military device for screening, signalling, and spotting. While first encountered on a significant scale in World War I, its importance was not realized until early in World War II when most of the data known at present were collected. In the last forty years the pace of research in smoke formulation has accelerated,[115, 239] both to defeat electro-optical devices in all wavelength regions, and to address the problem of toxicity. Screening smokes are generally white because black smokes are rarely sufficiently dense for screening. Signal smokes, on the other hand, are colored so as to assure contrast, and to be distinct in the presence of clouds and ordinary smoke.

Smoke has been found to aid the daytime observation of tracer projectiles and is also useful for tracking space vehicles during launch. Specific smoke tracers for training pilots have been produced (see Chapter 19). The .50-caliber M48 spotter-tracer was developed specifically in order to take advantage of the appearance of a smoke puff at the point of impact which happens to persist for a longer time than the flash.

Tiny liquid droplets are often called "mist" or "fog" and solid particles "smoke," but for purposes of obscuration and as signals, ordnance practice is to call all of them "smokes." These ærosolized substances exist in a wide range of particle sizes from about 1 μm to 10 μm radius. In smokes for obscuration or as signals, 0.5 to 1.5 μm is an optimal particle size.

Such small particles have a slow settling rate, acquire electric charges while moving through the air, exhibit Brownian motion, and, of course, are affected by air currents. Thus, a cloud of such particles in air acquires what may be called a fleeting persistence or "duration" (as distinguished from the duration of smoke emission from a smoke producing device). It hovers over the area of its creation but is removed and dissipated by wind or thermal updraft, generally before it can settle and before the particles can coalesce.

In military operations, the optical behavior of smokes and more recently the dispersion and dissipation of aerosols have become of great importance. If light of a given wavelength is shone on a smoke cloud the particles of which are of approximately the same size, and if the particles mainly reflect or allow its transmission, but do not absorb it, the result will be the almost complete scattering of the incident light. In sunlight, optimal conditions prevail when the light is neither in the line of sight with the observer nor directly opposite him, but at an angle of about 45°. The effect is one of screening from view objects and persons either in or behind the cloud of smoke or otherwise the aim is to notice the smoke cloud, puff, or trail as such.

The tactical uses of screening smokes and the means of producing them are of only limited interest to the pyrotechnist, since his devices can only be effective in a relatively small area. However, the second purpose of smokes – the emission of smoke clouds or trails as a means of signalling – is well served by pyrotechnic grenades, pots, or bursts, especially since various bright colors can be achieved in addition to white smoke.

Such actions as the envelopment of a ship or the hiding and protection of troops require large-scale and prolonged smoke emission. In an emergency and under favorable wind conditions, a ship may create a smoke cloud by deliberate maladjustment of its oil furnaces. However, contrary to what the layman may assume, the highly light-absorbing black soot particles and other types of dark smoke are less effective than white ones, as the particles in the dark smokes absorb light, rather than reflect it.

A minor use of screening smokes is the protection of orchards from sudden temperature changes by reducing the warmth lost by radiation, while at the same time the smudge pots furnishing the smoke clouds add some warmth to the area.

Obscuring smokes are effectively and least expensively made by heating and evaporating "fog oil," a cheap petroleum product resembling thin motor oil. White phosphorus (WP) has been measured as being 47 times as effective as oil-vapor. The obscuring agent is the combustion product phosphorus pentoxide (P_2O_5). White phosphorus burns rapidly and the heat of its combustion causes updrafts ("pillaring") that tend to negate the obscuring effectiveness. By converting the phosphorus under hot water into very small pellets (0.5 mm in diameter) and coating these with a viscous synthetic (GR-S)* rubber solution, a slower developing and hence less easily dissipated smoke is produced from this "plasticized white phosphorus" (PWP). Both WP and PWP are dispersed by bombs, grenades, or by artillery and mortar shell barrages.

Where screening smoke must be delivered by explosive action, and where at the same time smoke screens without fire hazard are desired, "FS" [a solution of 55 parts of sulfur trioxide (SO_3) in 45 parts of chlorosulfonic acid ($ClSO_3H$)], is cheap and effective though its screening power is only half that of phosphorus. "FM" ($TiCl_4$) is a more expensive product and offers no advantages. Both FS and FM become ærosolized droplets only in the presence of water and presumably display their power of obscuration best and fastest in humid air.

HC Smoke

The only type of screening or obscuring smoke that can be truly called pyrotechnic is the so-called HC type.

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* GR-S = Government Rubber Styrene. General purpose synthetic (styrene-butadiene) rubbers originally produced in government-owned plants as GR-S.

In World War I, Captain Berger of the French Army developed a mixture of zinc powder and carbon tetrachloride (CCl_4), which reacted strongly exothermically (0.6 kcal/g mixture calculated for the product zinc chloride in a gaseous state) to form zinc chloride as volatile hygroscopic droplets mixed with carbon. A modification of this mixture appeared in World War II in the United States as a Chemical Warfare Specification (CWS) composed of carbon tetrachloride, aluminum and zinc oxide, which was used in the AN-M8 HC Smoke Grenade. Because it excluded metallic zinc, it was much more stable, but the use of a thin volatile liquid such as carbon tetrachloride in a pyrotechnic item was undesirable. Other mixtures introduced the solid chlorine donor hexachloroethane (C_2Cl_6), called "HC," a term also generally used to describe the smoke mixtures containing it. It is a waxy solid, difficult to pulverize, and it has a high vapor pressure – but is a great improvement over CCl_4 in practice. The present formulations contain equal or near-equal amounts of zinc oxide and hexachloroethane (HC) with aluminum added in various percentages from 5.5 to 9.0. The percentage of aluminum can be chosen to affect the burn rate: under otherwise identical conditions, the above mixture with highest Al content burns 3 times faster than the lowest. The burning time also responds strongly to small amounts of additives such as zinc carbonate. The crystalline structure of the zinc oxide also has a significant rôle in determining the burning rate.

HC smoke mixtures react at a very high temperature, bringing the steel canisters to red heat, and create a luminous flame that may have to be concealed in some way for tactical reasons. The smoke itself is greyish-white, attesting to the presence of carbon. The amount of carbon is reduced when the aluminum content is low.

The reactions are complex[108] but one may assume there is a primary reaction between aluminum and HC followed by a reaction of aluminum chloride with zinc oxide, resulting in aluminum oxide and zinc chloride. Another hypothesis regarding the sequence of events assumes a primary thermitic reaction of aluminum and zinc oxide followed by interaction of the liberated zinc with the HC. In either case, the end result remains the same:

$$2Al + 3ZnO + C_2Cl_6 \rightarrow Al_2O_3 + 3ZnCl_2 + 2\,C$$

This corresponds closely to the formulation for the highest aluminum content (9%) for which a heat of reaction of 0.75 kcal/g of mixture can be calculated with $ZnCl_2$ at the standard solid state (otherwise the figure would be 0.54). If we reduce the aluminum content to one-third this amount, we arrive at the other extreme, a carbon-free reaction:

$$2/3\ Al + 3ZnO + C_2Cl_6 \rightarrow 1/3\ Al_2O_3 + 3ZnCl_2 + 2CO$$

However, a mixture with such low aluminum content yields only a calculated heat output of 0.32 kcal/g (0.10 for $ZnCl_2$ as a gas), and it is no surprise that this mixture burns erratically.

With the exception of the hand grenade, type AN-M8, which contains 500 g of HC mixture with a two-minute burning duration, HC smoke devices belong to the largest category of strictly pyrotechnic munitions. The M1 Smoke Pot (HC) contains 5 kg, the M5 Smoke Pot (HC) 15 kg of composition; in addition, they can be stacked for multiplication of the 5 to 20 minute period of smoke emission. First fires suitable for use with HC smokes are discussed in Chapter 12.

HC smokes are useful for small-scale or supporting screening action. The fumes are somewhat toxic but only slightly irritating, and cause no serious adverse effects for short periods of exposure. Smaller screening smoke devices are ideal for signalling. An example is the M15 Smoke Hand Grenade (WP) containing 400 g of white phosphorus – a fairly heavy-walled, bursting munition.

Testing of smoke mixtures for efficacy is difficult.[89] The best one can do is to compare various devices burning simultaneously in situations allowing similar air movement, by observation from an appropriate vantage point. A really objective test is the generation of the smoke under controlled and measured influx of air, drawing it through a test chamber where the amount of light scattering between a lamp and a photocell can be registered. The so called "standard" smoke is a smoke of such a density that a light of 25 cd intensity is just visible when observed through a layer of approximately 30 m. The amount of smoke agents required to produce one cubic meter of standard smoke is given in Table 20-1.

Colored Smokes

Inorganic-based smokes are rare for signalling, although they are used for other purposes (*e.g.*, rain making). It is possible to create colored ærosols by exclusive use of inorganic pigments or reactants, but they are generally less practical than the ones using organic dyestuffs. Pigment-grade red iron oxide has been used in explosive smokes. Shidlovskii[214] also mentions red lead, ultramarine blue and even cinnabar, the latter being very expensive and of high specific gravity. Pink and purple smokes can be produced from an iodate with selected reductants, but these are both expensive and high in weight/output ratio.

Special smokes, as might be useful in spotting munitions, can be made[161] from $KMnO_4$/Mg. Lancaster[139] and Ellern[70] report that black smoke can be made by the admixture of anthracene or naphthalene with potassium perchlorate, or with ZnO/Al/C_2Cl_6. Leenders[145] discusses smokes made with Mg/PCl_5 mixtures.

It is desirable for daytime signalling to have a variety of brilliant colors in the form of ærosolized organic dyestuffs or of inorganic compounds. These may be dispersed by evaporation and condensation of the coloring material, or explosive action, furnishing a puff of smoke. Obviously, a puff, streamer, or billowing cloud of bright red or orange coloration is not likely to be mistaken for incidental smoke from a bursting high-explosive shell or some burning matter ignited accidentally. Drift signals and float lights are used over water, and they emit both smoke and flame; similarly there is little chance of confusion.

The simplest way of dispersing dyestuffs having good heat resistance is by tamping the dye, mixed with 20% sodium chloride as an extender and coolant, into a shell, drilling a center hole, and filling it with a high explosive such as 67/33 Baratol.

According to information from the Research Laboratory of Picatinny Arsenal,* the disadvantage of large-scale destruction of the dye by heat from the explosion can be reduced, and the efficiency of color display improved, by reversing the arrangement of chemical components. In the colored shell XM152, the dye is in the center surrounded by salt, with the explosive charge in the outside layer. The smoke cloud results from the expansion following the implosive action.

The most important colored smokes – both for military and civilian use – are those in which the dyestuff is gradually evaporated from a mixture of dye and a pyrotechnic heat source. The heat source must be cool-burning and gas-forming in order to melt the dye while not decomposing it. However, the "recovery" may be no more than one-third of the amount of dye in the formulation.

Dyes that have been used in the United States because of their resistance to decomposition by heat and their capability to evaporate and recondense as a brilliant cloud or trail are enumerated in Table 20-2. The standardized smoke formulæ in Table 20-3 have been taken from a Picatinny Arsenal report which also gives a number of experimental formulæ, the variation in their burning times, and the persistence of the smokes produced. A number of other dyestuffs are mentioned in foreign literature, such as indigo, methylene blue, and rhodamine B.

Standard smoke compositions contain potassium chlorate and powdered ("confectioner's") sugar or sulfur as the oxidizer/fuel mixture and varying amounts of sodium or potassium bicarbonate as diluent and coolant. Thiourea has been used as the fuel in one instance; however, when this compound was used it seems to have made the mixture unduly heat-sensitive so that it "cooked-off" toward the end of a "hot-soak" at 70° C. In the U.S. patent literature, various special additives or substitutions to the basic colored-smoke formulations have been claimed. Processing aids such as kerosene (or a very thin lubricating oil) reduce the dust nuisance, improve compaction, and lessen the hazard posed by accidental ignition from friction.

Calcium phosphate promotes free flowing of the chlorate and sugar. In some formulæ, both the chlorate and the sugar are specified as containing 3% of magnesium carbonate for the prevention of agglomeration, which greatly aids in achieving good mixing. A little infusorial earth is effective in preventing lump formation in sulfur. Small amounts of such "inerts" – siliceous materials, iron oxide, graphite – are sometimes added because they promote an even progression of the reaction.

Besides confectioner's sugar, the more expensive lactose is occasionally specified and, exceptionally, other carbohydrates such as dextrin may serve as fuels. It is also possible to replace the chlorate with other oxidizers such as ammonium perchlorate but this is unusual, since the free hydrochloric acid from its decomposition may destroy some dyes.

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* Now known as the U.S. Army Tank, Automotive, and Armament Command, Armament Research, Development, and Engineering Center (ARDEC), Dover, New Jersey. For the sake of brevity, and sentimental attachment, the name "Picatinny Arsenal" has been retained in this book.

Notice that all colored smoke compositions contain potassium chlorate as an oxidizer. It is the only oxidizer which acts at low temperatures and assures the sublimation of the dye without reacting with it excessively.

After all that has been said about friction and impact sensitivity of mixtures of chlorates with fuels, especially sulfur, one wonders that such combinations are specified and can be processed on a fairly large scale. Thousands of tons of such mixtures were processed during World War II and again more recently. This indicates that the large excess of fuel material (including the organic dyestuff), and the addition of large amounts of pyrochemically inert and phlegmatizing sodium bicarbonate, greatly reduce the chances of accidental ignition from friction or other causes. These additions do not eliminate all danger. Especially during the initial phases of mixing, the distribution of the active materials may be favorable to ignition.

Another safety issue that must be raised involves the combination of potassium chlorate and ammonium chloride in a few smoke formulæ. This mixture is regarded as hazardous because an exchange reaction could form the unstable ammonium chlorate, which might become the cause of spontaneous ignition. Yet Shidlovskii vouches for the harmlessness of some of these mixtures, specifically of a composition for grey smoke containing 20 to 30% chlorate, 50% ammonium chloride, plus naphthalene or anthracene and a little charcoal. His explanation is similar to the one given above for chlorate/sulfur mixtures, *viz.*, the phlegmatizing effect of the large amount of a substance which is neither fuel nor oxidizer, in this case, the ammonium chloride.

The burning rate of a colored smoke mixture can be varied widely but is best kept in the range between 10 to 40 s/in. Increase in bicarbonate and dye content and reduction of chlorate content, in relation to sugar, reduce the burning rate. The theoretical chlorate/sugar ratio is 1.44:1 for the reaction to carbon monoxide:

$$4KClO_3 + C_{12}H_{22}O_{11} \rightarrow 4KCl + 12CO + 11H_2O$$

This yields 0.7 kcal/g (water taken as liquid), while the complete combustion yields carbon dioxide and proceeds at a ratio of 2.85:1:

$$8KClO_3 + C_{12}H_{22}O_{11} \rightarrow 8KCl + 12CO_2 + 11H_2O$$

Table 20-1.
Smoke Agents Required per Cubic Meter of Standard Smoke[240]

Phosphorus	0.063 g
FM + NH_3	0.095 g
Sulfur trioxide	0.10 g
FS	0.12 g
HC	0.13 g
FM ($TiCl_4$)	0.16 g
Oleum	0.16 g
Crude Oil	2.1 g

Table 20-2. Empirical and Structural Formulæ of Smoke Dyes

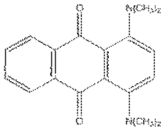
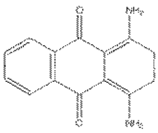
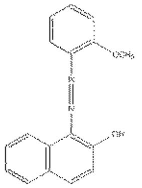
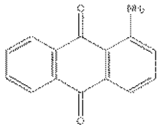
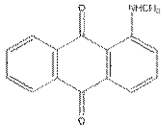
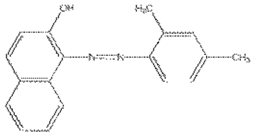
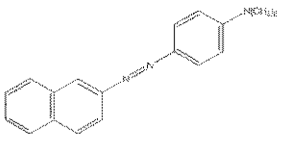
Compound	Formula	Structure
1, 4-*bis* (dimethylamino) anthraquinone	$C_{18}H_{18}N_2O_2$	
1, 4-diamino- 2, 3-dihydroanthraquinone	$C_{14}H_{12}N_2O_2$	
1-(2-methoxy) phenylazonaphthol	$C_{18}H_{16}N_2O_2$	
1-aminoanthraquinone	$C_{14}H_9NO_2$	
1-methylaminoanthraquinone	$C_{15}H_{11}NO_2$	
1-xyleneazo-2-naphthol	$C_{18}H_{16}N_2O$	
2-(4-dimethylaminoazophenyl) naphthalene	$C_{18}H_{17}N_3$	

Table 20-2. Empirical and Structural Formulæ of Smoke Dyes (cont.)

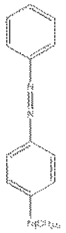
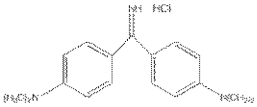
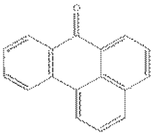
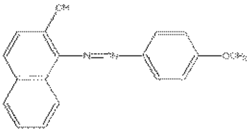
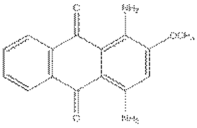
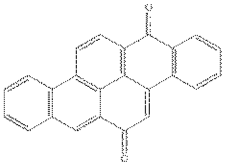
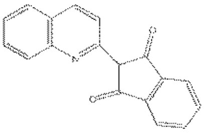
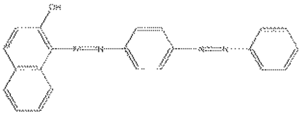
Compound	Formula	Structure
4-dimethylaminoazobenzene	$C_{14}H_{15}N_3$	
Auramine O	$C_{17}H_{22}ClN_3$	
Benzanthraquinone	$C_{17}H_{10}O$	
Disperse Red 1	$C_{17}H_{14}N_2O_2$	
Disperse Red 11	$C_{15}H_{12}N_2O_3$	
Indanthrene Golden Yellow G.K.	$C_{24}H_{12}O_2$	
Solvent Yellow 33	$C_{18}H_{11}NO_2$	
Sudan 3	$C_{22}H_{16}N_4O$	

Table 20-3. Typical Colored Smoke Compositions[25]

Red	1-methylamino anthraquinone	40
	Sodium bicarbonate	25
	Potassium chlorate	26
	Sulfur	9
Violet	1-methylamino anthraquinone	8.4
	Potassium chlorate	25
	Sodium bicarbonate	24
	1-, 4- diamino-2-, 3- dihydroanthraquinone	33.6
	Sulfur	9
Yellow XII	Solvent yellow 33*	42
	Potassium chlorate	22
	Magnesium carbonate	21
	Powdered sucrose	15
Green VII	Solvent Yellow 33*	12.5
	Solvent Green 3**	29.5
	Potassium chlorate	24.5
	Magnesium carbonate	17.0
	Powdered sucrose	16.5

* Solvent Yellow 33 is 2- (2-quinolyl) 1-, 3-indandione, "quinophthalone," known as "quinoline yellow."

** Solvent Green 3 is 4-di-p-toluidinoanthraquinone, also known as "quinizarin green SS."

Its heat output is 1.0 kcal/g. Since in smoke formulæ with sugar, the chlorate/sugar ratio is generally between 1:1 and 1.5:1 parts by weight, it is clear that there is a large excess of actual and potential fuel in the formula and hence a better chance for preservation of much of the dye. In formulæ with sulfur, the stoichiometric ratio of 2.5:1 chlorate to sulfur is commonly observed, but here a much larger addition of bicarbonate is customary. The reaction of potassium chlorate with sulfur furnishes about the same amount of heat as the sugar mixture, *i.e.*, 0.7 kcal/g of stoichiometric mixture.

Only scant data have been published on the heat of sublimation (or fusion plus evaporation) of smoke dyes. AMCP 706-187 gives 30.85 kcal/mol (130 cal/g) for 1-methylamino anthraquinone, a frequently used red smoke dye, and 28.9 kcal/mol (128 cal/g) for 4-(dimethylamino) azobenzene (Sudan Yellow GGA, Methyl Yellow, Butter Yellow). Shidlovskii[214] gives 26.8 kcal/mol (110 cal/g) for auramine, 21.2 kcal/mol (80 cal/g) for indigo, and 25.3 kcal/mole (180 cal/g) for paratoner. Combining the data for heat output from mixtures of chlorate with sugar or sulfur, and the heat requirements for the evaporation of the dye (disregarding other heat consumption factors), it is obvious that a large excess of heat is provided. Unfortunately, because of the flammability of the vaporized dye, this heat may suffice under unfavorable conditions to convert the bright, billowing colored cloud into a miserable, thin, greyish plume of burning dye. In most cases this fault occurs only as a temporary interruption of the smoke emission. In the case of grenades, it may be caused by dry grass catching fire from the hot fumes and igniting the dye, or from burning tape at the vent holes, perhaps even from an overheated metal burr at the orifice. In designs where an empty space exists between the top layer of the composition (plus first fire) and the orifice, the danger of ignition is reduced.

Colored smoke mixtures are compacted by the usual pressing techniques; the inevitable dust and consequent staining (of skin and equipment) make their manufacture very unpleasant.

More serious is the toxic and potentially carcinogenic character of several smoke dyes, such as Indanthrene Golden Yellow, the popular red dye methylaminoanthraquinone, and the much used auramine hydrochloride. This matter is discussed more fully in Chapters 2 and 3 of this book.

Experimental smokes have been formulated incorporating plastic binders in solution, in an attempt to minimize the hazards and nuisance factors; they have other advantages as well, such as increasing the dye recovery. In one type, intended for a drill mine signal, a small amount of binder in a large volume of highly volatile solvent forms a pourable slurry with composition that solidifies to a spongy mass after evaporation of the solvent. In another, well performing, formula for a little spotting charge, very firm small pellets compacted at only 400 kg/cm^2 from nearly dry granules of the mixture, give an excellent smoke. Future improvements in colored smokes, based on the conventional reaction mechanisms, may well lie in this direction.

Examples of munitions containing colored smoke mixtures are the M18 Colored Smoke Hand Grenade with 1,300 g of either red, green, violet, or yellow mixture and the M130 Yellow Streamer (hand-held) Ground Smoke Signal in which (as in certain light signals) a propellant charge is ignited by manual actuation of a primer and the device begins to produce a smoke streamer when it is only about 15 meters above the ground. The burning time is 10 seconds and the altitude reached is up to 250 meters.

The AN-Mk3 Mod 0 Marine Smoke and Illumination Signal contains both a flare and an orange smoke composition of about equal duration (18 seconds). However, only one signal must be initiated at a time. Canisters with colored smokes (or HC) can be expelled from Howitzer Shells M2A1 and M4, preferably close to the end of flight, whereupon the canisters continue along the same trajectory.

While there are a number of uses for colored smokes, the applications are fewer than of light signals. A hand grenade with a clay body mixed with dyestuff is used to mark persons in manœuvers, and is a color "signal" of sorts. Other forms of such personnel marking devices may be used as part of booby trap simulators, and, more recently, have been proposed for marking and identification of rioters. The dispersion of invisible marking material that appears under ultraviolet light has been suggested in addition to the use of dyestuffs. Colored and white smokes have also been tried for artillery tracers and more recently for the tracking of missiles.

Red and yellow are generally considered the most visible smoke colors, green as one of the least; against a background of vegetation in particular, green smoke may be nearly useless.

Since the purpose of signalling smokes is quite different from that of screening smokes, the previously described test method designed to measure obscuring power is probably not applicable to colored smokes.

Toxic Smokes

McLain[161] cites the admixture of DDT or of γ-benzene hexachloride to potassium chlorate and sucrose (58/19/23) for the killing of insects. Gopher bombs are generally not SO_2 generators (as suggested by Ellern[70]), because SO_2 is readily absorbed by the soil. Instead, a mixture of potassium nitrate and carbon is used in order to generate carbon monoxide.

Screening Infrared Images

Electro-optical sensors have brought about requirements for screening smokes which are effective against infrared sensors. The ability of an ærosol to screen infrared images is dependent upon several parameters, such as the surface reflectivity and the degree of dispersion of the ærosol. Flakes of aluminum or bronze 6-7 µm in size have been shown to have markedly higher extinction coefficients than does the traditional phosphorus pentoxide[239]. A contrary view is expressed in a Swedish study[115] which asserts that the screening action is derived mainly from the infrared radiation emitted from the cloud. Toward this end, at least in a high humidity environment, smoke from red phosphorus or the reaction between a metal and a chlorine donor (HC or FC type) are favored because these derive their smoke particles from the exothermic hydrolysis of metallic chlorides (Table 20-4).

Toxicity of Colored Smokes

It is now recognized that most of the dyes used in smoke generation are either carcinogenic in themselves or may contain carcinogens as impurity. The hazard arises not so much from field use as from handling of the carcinogenic materials during manufacturing or testing, as repeated exposure increases the risk.

The problem of replacement of the standard red smoke dye, 1-methylaminoanthraquinone, with the less toxic Sudan R [1-(*o*-methoxyphenylazo)-β-naphthol] has been considered[25] but not yet implemented. The problem of carcinogenic products of combustion is also inherent in diaminodihydroanthraquinone, found in the purple dye, which easily oxidizes to 1,4-diaminoanthraquinone, closely resembling the red dye. The necessary characteristics of a replacement for the standard red dye were thoroughly examined by Vigus and

Table 20-4. White Screening Smoke Compositions

	Burning Types[59]		Imploding Type[60]
Magnesium	11	13	11
Manganese dioxide	–	–	30–34
Zinc oxide	46	47	3
Red phosphorus	–	–	38
Polyglycol resin	11	8.7	8.7
Epoxy resin	6.8	5.3	5.3
Lead dioxide	–	–	4
Dechlorane	25	–	–
Hexachlorobenzene	–	26	–

Deiner,[243] who conclude that the only candidates acceptable from standpoints of performance and lack of toxicity are 9-diethylaminorosindone and the aforementioned Sudan R.

Dispersion of Chemical Agents

In a manner that closely parallels the creation of ærosols for obscuration or signalling, one can also form ærosols of chemical warfare agents. As a rule, the agent is mixed with a heat- and gas-producing pyrotechnic mixture, but there are cases in which the agent is actually a reaction product of the heat-producing system. Arrangements where a gaseous heat source or gas itself furnishes a separate dispersing force are treated in Chapter 22 under gas generators.

Dispersion of chemical agents by pyrotechnic means has advantages and disadvantages. Where the tactics of dissemination require a multitude of relatively small, discrete units, and in particular where the area is not directly accessible to the invading forces, the self-contained, compact and reliably functioning pyrotechnic canister or grenade is preferable. A large amount of the agent may be destroyed in the process, but, as is the case with regular signal smokes, this loss is often acceptable. In this respect, the techniques parallel the dispersion of signal smoke. Dissemination over large areas, comparable to that of screening smokes, cannot be performed economically by such chemical mixtures, and purely physical dispersion is the better solution; this is the case with crop dusting.

The agents considered for pyrotechnic dissemination are pesticides and fungicides, irritants for riot control and warfare, and highly toxic substances such as "nerve gases." To these must be added certain crystalline cloud-seeding substances that promote precipitation of moisture from the air and are useful for rain-making, hail prevention, fog dispersal, and even breaking up hurricane formations. The production of disinfectant gases such as sulfur dioxide will be treated in this chapter as well.

As to the means of dispersion, the principles and practices of cool-burning compositions for colored smokes apply to the dispersion of other agents with only slight variations in formulation.

Dinitrosopentamethylenetetramine is remarkable "monopropellant" of cool and often flameless exothermic decomposition slightly above its melting point of 203° C. It was originally developed in Germany as a "blowing" agent for rubber, but has been used in mixtures with pyrethrum, γ-BHC or DDT.

Shidlovskii[214], citing Russian and British references, divides the agriculturally useful thermal mixtures into insecticides, in which γ-BHC, DDT, and others are combined with chlorate and anthracene, dicyandiamide, or hexamine; fungicides with 2,3-dichloro-1,4-naphthoquinone (Dichlone, $C_{10}H_4Cl_2O_2$) as the active agent; and acaricides (mite control agents) using a compound named tedion (tetradifon, $C_{12}H_6Cl_4O_2S$) in a chlorate-fuel mixture.

Irritants which affect the mucous membranes of the eyes and the respiratory system are used in war and police work to force people out of hideouts or to disperse crowds. Chloroacetophenone (CN) has long been an effective tear gas (lachrymator) and lends itself to dissemination by heat when mixed with sugar, potassium chlorate, potassium bicarbonate, and diatomaceous earth, as in the M7A1 Tear (CN) Hand Grenade. The effect of CN* can be enhanced and prolonged by mixing with the vomiting and sneezing agent (sternutatory) diphenylaminechloroarsine or Adamsite (DM), as used in the M6 Irritant Hand Grenade, CN-DM. This device employs smokeless powder as the heat source and propellant and magnesium oxide as a diluent. The particles are coated with boiled linseed oil and further coated with precipitated chalk and nitrocellulose; the granules are then highly compacted.

Recently, these agents have been replaced by the compound *o*-chlorobenzylidinemalononitrile, coded CS, as in the M7A3 Tear Hand Grenade CS. Because of its sensitivity to decomposition, this material is mixed with sugar and a little wax and water, compressed in pellet form coated with sugar syrup, and dried. The pellets are then embedded in a modified chlorate/sugar composition. In another technique, the powdered CS is enclosed in gelatin capsules, which are mixed with the same or a similar heat powder combination.

Irritants can also be dispersed by explosive force, as in the baseball-sized M25 Riot Hand Grenades, which are filled with CN or CS. The grenades are made of plastic to avoid lethal fragments.

The above-mentioned agents, while unpleasant even in minute concentration and extremely distressing in larger doses, generally leave no lasting after-effects. Soon after removal from the contaminated atmosphere, complete recovery from the effects of CS is prompt, but as little as 1 mg of CS per cubic meter of air will irritate the eye. This is less than one thousandth (and perhaps as little as one ten-thousandth) the threshold value for chlorine or sulfur dioxide. The psychological after-effect of exposure to CS is remarkable: a person who has been exposed to it, even though the exposure was not extreme, may relive the burning sensation on the lips, tongue, and nose merely by thinking about it.

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* This designation has nothing to do with the chemical symbol CN for the cyanide radical.

Lethal agents, such as the "poison gases" of World War I, have always been dispersed by explosive action, with the exception of the original chlorine gas attack of 1915 at Ypres, where commercial cylinders were used.

Turning from the nastier aspects of pyrotechnic applications to something more constructive, the field of creating ærosols to cause condensation of rain clouds and fog is now considered.

Crystals of silver iodide (AgI) resemble ice crystals quite closely, both belonging to the hexagonal crystallographic system. As such, they can form nuclei for the condensation and crystallization of water in a super-cooled and hence supersaturated moisture-laden atmosphere. Lead iodide (PbI_2) behaves similarly, and the organic compounds metaldehyde and phloroglucinol (1, 3, 5-trihydroxybenzene) have demonstrated activity in the laboratory.

Two variations of dispersion are possible: the iodides may be present as such and dispersed by a mixture of the composite propellant type; or the iodide may be produced chemically, via one of several methods. Shidlovskii[214] cites mixtures of lead powder with iodine donors such as ammonium iodide, iodoform (CHI_3), or "iodanil" ($C_6O_2I_4$) mixed with propellant material. The iodates of silver and lead have been used as oxidizers with gas-forming binders and heat-producing fuel metals.

While interest in the United States has focused on the aborting of hurricanes and to a lesser extent on rainmaking, it appears that the major Russian interest is hail prevention. A secondary effect of causing precipitation by cloud-seeding is the removal of clouds and fog.

Snow avalanches prevalent in the Rocky Mountains are caused in part by sublimation of the lowest snow layers with formation of weak fragile layers of crystals. This "depth hoar" may cause the whole mass of snow above it to break off in great slabs. Traces (a few grams per cubic meter) of long-chain organic molecules such as 2-octanol, or the compounds benzaldehyde, n-heptaldehyde, and (less effectively) ethylene glycol inhibit ice crystal growth by sublimation and thus preserve a strong bottom layer of snow. The effectiveness of avalanche control by dissemination of such chemical agents has not yet been conclusively proven. However, it is obvious that pyrotechnic dispersion of such chemicals would be an ideal way of spreading out these materials in finely distributed form on remote or steep mountainsides just prior to the first snowfall, by dropping canisters or shooting rifle grenades or artillery shells in areas where potentially hazardous snowbanks form.

A recent application for pyrotechnics has been the dispersion of metals and their compounds at high altitude (of 80 km or more). While one cubic kilometer of air at atmospheric pressure weighs one million tons, the same volume at 150 km altitude weighs no more than 2 kg! In such a rarefied medium, sodium vapor dispersed from a rocket will create a large brilliant yellow train visible at twilight, useful for the study of ionospheric winds and temperature. The sodium release has been performed by the heat from 8 kg of thermite evaporating 2 kg of sodium powder mixed with the thermite, at a temperature of 900° C. Oxidation of the sodium takes place slowly at such altitudes. An important modification of this technique is the replacement of sodium by barium. This allows the creation of barium ion-electron plasma suitable for the study of magnetic field lines. Potassium and cæsium have also been employed for certain explorations. As mentioned earlier, the formation of ions from these metals also takes place in high-energy flare mixtures and in rocket propellants when the alkali comes from oxidizer salts.

The explosive dispersion of aluminum or the release of trimethyl aluminum at high altitude leads to formation not of the familiar Al_2O_3, but of the lower oxide, AlO, which emits a blue glow useful for temperature measurements. Other studies with different goals involve the release of ammonia or nitric oxide.

Chapter 21

Generation of Sound

Sound generators have military applications as warning and signalling devices and for the training of troops through simulation of the effects of live ammunition. Pyrotechnic devices may be used to create battlefield sound and light flashes less expensively than can ordnance, and single burst and whistling sounds can both be produced in a single device. Either air burst or ground burst effects can be obtained. Air burst simulators mimic the explosion of artillery rounds. They produce a flash, a puff of smoke and a loud report. Ground burst simulators incorporate the whistling effect of incoming artillery rounds.

Formulæ and reaction characteristics of various sound-producing pyrotechnic mixtures are listed in Table 21-1.

Pyrotechnic means of creating sound include the "joyful noise" of explosive fireworks items described in Chapter 15 and whistling devices. The latter are found in fireworks for pleasure as well as in a few military items. The strictly utilitarian explosive sound producers are sometimes identical with fireworks items. They are parts of weapon simulators that make manœuvres more realistic, and can actually be used for deception of real enemies; a few have been tried as crop-protecting bird deterrents and for clearing airport landing strips of hovering birds; others represent a commercial article in the form of warning signals such as railroad torpedoes. Various combinations are used for simulation of noises and other effects on battlefields and for various catastrophes in the motion picture industry. Military salutes might also be included, though their design differs from that of the other devices.

Military training devices employ flash and explosive sound as in the Gunflash Simulator (see Table 21-1) in which a whistling sound precedes the flash and explosion, and the M117 Booby Trap Flash Simulator. In fact, all flash signals function also as auditory signals if operating at a distance not much exceeding 2000 meters.

The M80 Firecracker (and the apparently quite similar Navy Mk1 Mod 0 One-Inch Salute) are the military counterparts of the civilian "salute" – a small cardboard cylinder with a piece of visco safety fuse giving about three seconds delay. A typical flash cracker mixture contains aluminum, sulfur, antimony sulfide, and potassium perchlorate. The crackers may be attached to a variety of pull or pressure initiators. For the purpose of military protocol, as well as for simulated heavy gunfire, various sizes of primed gun cartridges are partially filled with

Table 21-1. Typical Sound Producing Formulæ[160]

	Booby Trap Flash Simulator	Whistling Booby Trap	Gunflash Simulator	Ground Burst Simulator	Air Burst Simulator
Magnesium, Grade A, Type 1	17	-	45	34	-
Antimony sulfide, Grade 1, Type C	33	-	-	-	-
Potassium perchlorate	50	73	35	40	-
Gallic acid	-	24	-	-	-
Red gum	-	3	-	-	-
Barium nitrate	-	-	15	-	-
Barium oxalate	-	-	3	-	-
Calcium oxalate	-	-	1	-	-
Graphite	-	-	1	-	-
Aluminum, flaked, Type 1	-	-	-	26	9
Black powder	-	-	-	-	91
Autoignition Temperature, °C	562	453	596	762	300

"Amorces" are percussion sound generators, also called toy caps. Paper strips are "imprinted" with evenly spaced dots which are then covered with gummed tissue paper. The active components, potassium chlorate and red phosphorus, are moistened *before* mixing with water containing gum arabic or dextrin. Sulfur and precipitated chalk are added as phlegmatizers. More was said about the danger of mixing potassium chlorate with red phosphorus in Chapter 13.

black powder either in loose form or as compressed pellets. A felt wad and a closing cup confine the powder charge; obturation of the developed gas and the subsequent sudden expansion help in producing a loud noise. Such a powder charge may be quite substantial; in the Blank Ammunition Double Pellet Charge for 75 mm Guns or Howitzers, the two pellets combined weigh 400 grams.

Since the advancing motion of a railroad engine's wheel on a steel rail is comparable in effect to a glancing sledge hammer blow, a tablet of an interposed impact-sensitive pyrotechnic mixture will explode with a report loud enough to be heard in the engine cab above the other noises. In the domestic form of the well-known railroad torpedo, a chlorate-containing mixture compressed in the form of a rather substantial pellet with flat bottom and rounded top is wrapped in moisture-resistant paper. Sand particles glued to the bottom and a pair of lead or aluminum straps hold the item firmly onto the rail – an important feature, since the torpedo must not be dislodged in severe rain or windstorms.

These torpedoes are handled rather casually, and their impact sensitivity must not be excessive. In testing, a 25 lb drop weight of a certain profile is used, which must not set off the explosive mixture when dropped from a height of 20 cm but must function (at least on the second try) from 40 cm. The sound level at a distance of 6 m should be no less than 105 dB. The torpedo must not disperse any damaging fragments (as evidenced by its effect on a denim cloth at 1 m), and conditions of water and heat resistance are prescribed by commercial convention. Certain foreign railroad torpedoes contain a black powder charge confined in a metal capsule and are actuated by a primer.

Explosive sound rarely evokes a question about the actual mechanics of its propagation as an unwanted by-product of the sudden expansion of propellant gases in firearms or of explosive action in blasting. The subject seems to be generally ignored in books on sound. It only appears rarely in the special literature when methods for attenuation are sought where the sound is carried from the test site through the air and through the ground to a populated area. While the subject is of interest to the pyrotechnic manufacturer either in connection with photoflash cartridge testing or while he is engaged, additionally, in some explosives work, it will not be more than merely touched upon here. One method used in gun silencers is to absorb some of the sound waves with fibrous materials of the highest possible density, such as steel wool. Muzzle attachments may also contain metal baffles. By the same token, heavy steel curtains or sand- and water-filled enclosures act similarly on explosives test sites.

Oscillating or Pulsating Reactions

The most commonly used fuel in pyrotechnic whistles at present is probably sodium salicylate. Sodium and potassium benzoates are also popular. These have mostly replaced the 3:1 mixture of potassium chlorate and gallic acid, which is expensive and quite sensitive to friction and impact. Also largely abandoned is the first material found useful for pyrotechnic whistles, potassium picrate. This functioned either alone (yielding in addition to the whistling noise a plume of black smoke) or in conjunction with potassium or barium nitrate, which serve as oxidizers for the excess carbon, so cutting down the smoke. Potassium 2-, 4-dinitrophenolate, with its similarity to the picrate, has also been advocated, as has potassium hydrogen terephthalate (benzene-1,4-dicarboxylate). The extent to which these substances have found applications on a commercial scale appears to be limited.

Typical whistle formulæ are given in Table 21-2. Caution is advisable with these highly active mixtures. All are very sensitive to shock and friction, and explosive even in moderate quantities. Of these, however, the potassium benzoate composition appears to be the safest.

Maxwell's article[157] mentions the interesting fact that a pyrotechnic whistle not only burns well under water, which is to be expected, but also that the sound can be heard above the water, though at greatly reduced intensity.

A propellant actuated device could undoubtedly be used to produce a whistling noise or the noise of a siren by acting strictly as a compressed gas source for a suitable acoustical device. This is of little apparent interest, given the existence of purely pyrotechnic whistles.

Studies of whistles are few,[199, 253] but like other pulsating reactions they depend on the variation in reaction rates encountered in layerwise reactions. Changes in the burn rate are due to a variation in mechanism. The frequency of the sound depends partly on the length of the tube in which the mixture is burned, varying in one case from 5000 Hz at 1 cm to 1600 Hz at 7 cm. Maxwell holds that the composition must be contained in a resonating tube so that the flame will be forced in and out of the surface by alternate waves of compression and rarefaction.

A somewhat different mechanism is suggested by Wasmann[247] in his studies on pulsating (strobing) composition (examples in Tables 21-3). He hypothesizes multiple competing reactions involving magnesium/aluminum alloy (magnalium) and an inorganic oxidizer: the magnesium is oxidized in a "dark" (non-luminous) step, then the aluminum is rapidly oxidized by nitrogen oxides giving a flash of light. Gol'binder proposes a different mechanism in his studies[92]; it is dependent on physical movement rather than chemical reaction for the observed delay. For example, one of his compositions is methyl nitrate in a polymethacrylate matrix; the reaction takes place by the methyl nitrate boiling up to the surface where it explodes giving noise and light. Thus the pulsating burning is controlled by the heat flow from the hot surface of the interior of the mixture. Wasmann[247] describes a hybrid system which employs alkaline earth perchlorates in the matrix. These products smolder for quite long periods of time before giving a loud explosion and a flash of color (*e.g.*, $Sr(ClO_4)_2$ gives a red flash). The products are of little practical interest as they burn for long periods of time, frequently blow themselves out, and readily absorb water because of the hygroscopic nature of the anhydrous perchlorates.

Pulsating reaction mixtures were discussed by Shimizu in an article which he submitted in March of 1980 to A. Pokorny in Toulouse, France. In part, freely translated, he says:

Table 21-2. Traditional Whistling Compositions[247]

Potassium chlorate	75	-	-	-	-	-
Potassium perchlorate	-	-	70	-	72.5	-
Potassium nitrate	-	50	-	30	-	37
Gallic acid	25	-	-	-	-	-
Potassium picrate	-	50	-	-	-	63
Potassium benzoate	-	-	30	-	-	-
Potassium dinitrophenolate	-	-	-	70	-	-
Sodium salicylate	-	-	-	-	27.5	-

> "The problem is one of obtaining good pulsating colors. This can be achieved by replacing the magnalium with magnesium, but then one must guard against the corrosive action of the ammonium perchlorate. Corrosion protection is afforded by the admixture of a small quantity of potassium dichromate. Stars containing ammonium perchlorate are hard to ignite unless black powder formulated with sodium nitrate is used as igniter.
>
> "The quenching of the color flash is caused by being washed out by the alumina in the flame. Therefore in order to improve the color, one must get rid of the aluminum in the formulation."

Pulsating color compositions which meet Shimizu's criteria are shown in Table 21-4. The pulsating frequency ranges from 0.5 to 10 Hz, the higher frequencies being associated with higher percentages of magnesium. Shimizu has discussed pulsating reaction mixtures in detail using copious illustrations and triangular graphs[167].

The reader must distinguish these pulsating reactions from the "tremalon" or "glitter" effects seen in fireworks, which was exhaustively reviewed by Winokur[256], and which is due to viscous droplets dispersed for variable distances behind a burning star prior to their flashing. The formulations typically consist of gunpowder or its ingredients, flaked aluminum, and antimony sulfide; for more information see Chapter 15.

Table 21-3. Pulsating Pyrotechnic Systems[247]

	White	Red	Green
Barium nitrate	65	-	60
Mg/Al alloy	20	18	20
Nitrocellulose	7	-	5
Ammonium perchlorate	5	6	7
Sodium oxalate	3	-	-
Strontium nitrate	-	65	-
Dicyandiamide	-	8	-
Potassium perchlorate	-	3	5
Barium perchlorate	-	-	3

Table 21-4. Improved Pulsating Compositions

	White	Yellow	Green	Green	Orange	Red
Magnesium	10-50	20-30	20	10-50	20-50	20-40
Ammonium perchlorate	by difference					
Sodium nitrate	-	10-30	-	-	-	-
Barium nitrate	-	-	10-20	-	-	-
Potassium perchlorate	10-20	-	-	-	-	
Barium sulfate	-	-	-	10-20	-	-
Calcium sulfate	-	-	-	-	10-20	-
Strontium sulfate	-	-	-	-	-	10-20
Potassium dichromate	5	5	5	5	5	5

Chapter 22

Gas Generators and Heating Devices

In civilian life, in industry and in a few specialized military applications, apart from ignition or destruct systems, it is sometimes convenient to have an intense, self-contained, instant heat source available. This type of pyrotechnic gadgetry has been encouraged by the development of "gasless" heat compositions. These can be confined in fully sealed cartridges, whereby heating not only takes place without flame or sparks, but more heat can be transferred in orderly fashion without losses through vent holes. Even where such efficiency is not possible or not needed, and the heating process is rather uncontrolled, as in some applications in welding or foundry practice, the capacity to bring heat to any spot without the necessity of power lines, gas burners, or welding equipment, can be a great convenience.

Examples of non-destructive applications of pyrotechnic heat are the heating of canned foodstuffs, or of water for the preparation of food, by sealed heat cartridges or in double-walled cans; the activation of galvanic cells with solid, fusible electrolytes; auxiliary heat sources for other types of galvanic cells; heat cartridges for soldering irons and heat sources for comfort in cold weather; means for welding wires; and heat applications at various levels of intensity in foundry practice to prevent cooling of top layers of melts or of so-called risers.

Ellern[70] mentions the use of quicklime and water as a heat source for food cans. This reaction furnishes 0.26 kcal/g (CaO), and while not classifiable as pyrochemical, it is said to be able to produce a temperature as high as 450° C – enough to set fire to guncotton, sulfur, or wood.

Mixtures containing iron powder, water, sawdust and activated charcoal in air-permeable bags are marketed as heat pads for hand and body warming in winter (U.S. Patent No 4,408,355). The United States military has adopted a similar device for heating soldiers' rations in the field. The heater is composed of a magnesium-iron alloy dispersed in plastic powders, and is activated by pouring water on it.[179]

It is possible, without resorting to the use of highly refractory metal as an envelope, to design a heat cartridge that will heat water to near boiling in seconds, provided that the greater part of the tube remains submerged in the water. The strong quenching effect prevents the steel body from melting and since no consideration of scorching arises, such a concentrated heat source is occasionally permissible.

One commercially available, practical pyrotechnic heat source is the fully enclosed, primer-activated cartridge. Mixtures of zinc, barium chromate, and manganese dioxide are said to be the heat-producing substance. A soldering iron is marketed in the United States that uses such a cartridge activated by the pull and release of a spring-loaded pin. The inexpensive cartridge furnishes 10 kcal and is of merit for use in isolated areas where electrical current is unavailable or use of a torch flame for heating is impractical or hazardous.

Also worthy of mention is the heating component of self-vulcanizing tire patches, consisting of a cool and slow-burning mixture of potassium nitrate and a carbonaceous material such as sugar with some binder.

The activation of solid-electrolyte cells (thermal batteries) using gasless heat compositions has received a large amount of attention. Ongoing work is reported biannually in the International Power Sources Symposium, the proceedings of which are published by the Electrochemical Society. Thermal battery electrochemical cells consist of an alkali or alkaline earth metal anode, a fusible salt electrolyte, and a metallic salt depolarizer. The pyrotechnic heat source is usually inserted between cells linked in series for rapid activation. The term "thermal battery" does not refer to a single electrochemical system but to a family of cells. The electrodes, the electrolyte and the battery design vary according to the performance desired. Most thermal batteries use molten lithium chloride-potassium chloride eutectic as the electrolyte (m.p. 352° C). The two principal pyrotechnic heat sources used in thermal batteries are a paper-type composition of zirconium and barium chromate powders supported on inorganic fibers, and a pressed tablet made up of iron powder and potassium perchlorate.

The $Zr/BaCrO_4$ "heat paper" is manufactured from pyrotechnic grade ingredients, both having particle sizes of about 1 to 10 μm. Inorganic ceramic fibers are added. The mixture is formed into "paper" as individual sheets by a paper-making process. The resulting sheets are cut and dried. Once dry, they must be handled very carefully because they are very sensitive to static electricity. Heat paper has a burning rate of about 10-15 cm/s and a heat output of about 400 cal/g. Heat paper burns forming an ash with high electrical resistance. Therefore, it requires the use of a nickel or iron electrode and intercell connectors.

Fine iron powder and potassium perchlorate are blended dry and pressed to form heat pellets. The iron content ranges from 80 to 88% by weight and is considerably in excess of stoichiometry. Excess iron provides the reactive pellet with sufficient conductivity so that intercell connectors are not necessary. The heat output ranges from 250 to 350 cal/g. Burning rates are much slower than those of heat paper and the ignition energy required is higher.

Thermal batteries are initiated either by a percussion-type primer or by an electrical pulse to a squib. Heat pellets often require an intermediate heat paper firing train to carry the ignition from the squib to each pellet.

The value of a solid electrolyte battery derives from the fact that the ordinary galvanic cell undergoes chemical reactions whether in use or in storage, whereas the heat battery is completely dormant until the moment the electrolyte is melted. This advantage is somewhat balanced by the transient output of current.

Further, such "one shot" devices suffer all the inherent difficulties of establishing reliability data that that term implies.

Pyrotechnics plays a more subordinate role in other galvanic cells of high storage life where the inactivity is achieved by separation of the battery proper and the electrolyte. In ammonia-activated batteries, pyrochemical heat aids in transfer of the ammonia, and in certain alkaline batteries, a concentrated potassium hydroxide solution is projected into the battery cavity with the help of a propellant-gas cartridge.

At low ambient temperatures, dry cells and other galvanic cells suffer a voltage drop under load, due to polarization. Pyrotechnic heat sources can be employed to remedy this problem. Experimentally, one such system consists of cheap, easily molded, relatively cool-burning pellets, inserted into metal tubes, which are immersed in the electrolyte. The pellets consists of fine iron powder and sulfur (64/36%). They are easily ignited and glow at a bright red heat.[241]

In United States foundry practice, exothermic compositions called "hot topping compounds" are used. If a thermite reaction is to be used as the heat source, it must be modified in such a way that instead of separating into liquefied layers, the whole reacting mass sinters and stays in place. This is achieved by replacing all or part of the aluminum with magnesium, the highly refractory oxide of which permeates the liquefied mass. Such a composition is said to be useful for the welding of aluminum or aluminum-alloy wire cables. Along the same lines, Shidlovskii[214] emphasizes, as shown by several drawings in both his second and third editions, the usefulness of "magnesium thermite" for welding telephone and telegraph wires. He describes a cylindrical pyrocartridge, longitudinally perforated and slipped over abutting wire ends while they are temporarily held together by a clamp. He also quotes the composition of a special thermite said to be used to weld ground wires to metallic structures. An American device used for the same purpose is sold under the trade name Cad-Weld. When using it, the ground wire is inserted in a hand-held unit resembling a bullet mould; then the welding mixture and igniter composition are added. The mould must be held in place for about a minute to allow the metal to solidify. In the future, welding or brazing by means of a small, self-contained heat source may well be used for construction and repair in space.

Gas Production

There are three functions of pyrotechnic gas production: high-pressure gases (which perform mechanical work); production of chemicals such as nitrogen, oxygen, or sulfur dioxide; and the dissemination of irritants or toxins.

High-pressure gas producers perform mechanical work such as propelling a projectile or rocket, pushing a piston or driving a turbine. Such mixtures should be safe to handle, easily ignitable, economical to use, non-hygroscopic and produce a fairly large quantity of gas from a small package. Black powder was first used as the primary high gas pressure producer but it has been replaced by other mixtures because black powder leaves a large fraction of solid residue on burning.

Gas generators differ from gas-actuated devices only in their output. There are basically two kinds of devices: those of short duration, called initiators, which produce gas only for milliseconds; and those of longer duration lasting up to several minutes. The distinct characteristics of these systems is that they produce high pressures ranging from a low of 4 MPa to a high of 12 MPa. Such devices are used for driving turbines, ejectors, cutters, and thrusters.

Pure gas production by pyrotechnic means may be desirable because the device is small and replaces the need for high-pressure storage bottles.

The science and techniques of gun propellants, rocketry, and explosives are separate disciplines, though together with pyrotechnics they have a common pyrochemical basis and involve overlapping phenomena. As a matter of practice rather than of formal classification, the following uses of pyrochemcially-produced gases are generally regarded as being in the area of pyrotechnics. Moderately-sized and simply-built rockets, cardboard mortars, or integral parts of items that propel fireworks or military signals into the air are always regarded as pyrotechnic components. Subminiature rocket projectiles and very small control rockets for steering missiles and spacecraft in flight may or may not be considered as belonging to this category.

Cartridge-Actuated Devices (CAD), now preferably called Propellant-Actuated Devices (PAD), are used for ejection of stores from dispensers or aircraft, and for the complex mechanisms of ejection of pilots from fast-flying aircraft or astronauts from spacecraft in cases of low-altitude aborts. The major devices are classed as removers (retractors), thrusters, catapults, guillotine-type cutters, and certain initiators (for operation of other PADs).

Gas generators for pressurization operate hydraulic accumulators; activate galvanic cells by forcing alkali solutions into the actual battery; operate fire extinguishers, turbo-blowers, and electric generators; and inflate balloon-like flexible cells such as emergency flotation bags for military helicopters. They may also act as dispersants for finely powdered solid agents (of the type described in a preceding chapter) or of solutions. In such applications it often appears to be desirable greatly to constrict the gas flow from the cartridge. Here, the orifice is kept so small that delivery of gas proceeds essentially independently of the geometry and resistance of the secondary device. This is called a "high-low" system. While it has the advantage that the gas flow can be predetermined and tested independently, the heat losses are large so that more than two and a half times as much propellant is required as in standard PADs. A further disadvantage is the possible obstruction of the small orifice by unburned propellant slivers or debris from the initiation system. The design considerations for PADs in terms of sizing and performance were reviewed by Pollard and Arnold[192].

Guillotine-type cutters are part of escape and stage separation systems, since they sever wires or cables preparatory to implementation of the principal operation. Such cutters function in recovery systems to cut parachute shroud lines, load lines suspended from high altitude balloons, or anchoring cables of a submerged moored mine.

Explosive switches are devices in which the electrically initiated explosive prime ignition charge, assisted by a propellant powder, moves a piston, opening and closing electric contacts. Similar action is produced by dimple motors, pistons, or bellows. Dimple motors work by inversion of a curved flexible disk. The movement effected may be as small as 1 mm in a dimple motor against a 4 kg load, 8 mm in a piston motor against 10 kg, or 2.5 cm in a bellows motor to move as much as 50 kg. In the same group belong explosive valves, which allow nearly instantaneous opening or closing of a channel through which gases or liquids can flow. Perhaps the word "explosive" in such items is a misnomer since the small amount of primary explosive acts without destructive effect, in the manner of a fast propellant. Added propellant powder may do little more than maintain pressurization and prevent reversal of the piston. Explosive valves are part of automatic inflation devices on certain life vests, such as those for astronauts. Actual explosive force is employed in *explosive bolts* and nuts. Here, efforts are made to channel the explosive force inside a cavity toward a predetermined weak spot in order to effect a clean fracture. These items serve the purpose of stage separation of multistage missiles. Some act by means of a cutting action from a linear shaped charge and others by the expansion of a closed volume which causes fracture at a predetermined location. Choice of the type may depend on whether fragmentation can be tolerated or not.

The development of PAD started prior to World War I, and research and development between the two wars included civilian uses, such as the design of a humane cattle killer with a cartridge-operated captive bolt, as well as military applications. The greatest boost to the modern PAD came, however, from the need for systems that ejected pilots from fast-flying aircraft. This problem was given to the Ordnance Corps in 1945 and, together with other parallel efforts, led to various systems and designs of actuating devices.

The concern addressed here is mainly the pyrochemical means of obtaining gas from solid compounds or mixtures. Some details follow on the most important gas-forming substances and combinations, *i.e.*, black powder, nitrocellulose powders, high nitrogen propellants, composite propellants, and high-temperature propellants. All of these are in practical use and are either specified for standardized cartridges or are in the process of replacing older propellants.

Black powder (gunpowder), the jack-of-all-trades of the fireworks art, is characterized by versatility, low cost, easy ignitability, excellent fire transfer properties at a wide range of temperatures and pressures, and a good stability at elevated temperatures. It is, however, difficult to adapt to orderly slow burning progression, is low in gas output, high in corrosive residue, and its smoke is more likely to be detected by surveillance. Its manufacture is relatively hazardous and specialized. Smaller amounts under good housekeeping conditions are fairly safe.

Black powder is principally manufactured by the wheel-milling process, much as it was two or more centuries ago, although alternate means have sometimes been advocated. The individually pulverized saltpeter, charcoal and sulfur are intimately incorporated in the presence of a small amount of moisture. The milled material is then pressed, and the resultant "press cake" is corned (granulated). After finishing and polishing, the powder is usually coated with graphite (glazed); then it is graded – separated into various grain sizes. Of the nine classes of fineness (detailed in MIL-P-223B), Class 1 is the coarsest and Class 8 the finest powder, while Class 9 is called sphero-hexagonal with a complex shape of 1.5 cm diameter, each grain weighing 3.54 g.

The Army numbers are from A1 for the coarsest to A6 for the finest; the Navy names are Cannon, Musket, FFG, Shell, and FFFG to about 50 mesh, and Class 6; while the grades Fuze, FFFFG, and Meal correspond to Classes 7 and 8.

The specific gravity of the coarser grains must be 1.69 – 1.76 for unglazed, 1.72 – 1.80 for glazed powder[70].

Charcoal is not pure carbon but rather presents an undefined intermediary state between its organic origin and the element carbon, retaining both hydrogen and oxygen. Because of this composition and its high absorption capability, it contains as much as 6% water; black powder specifications allow, therefore, a maximum of 0.70% moisture. The equilibrium water content varies with the relative humidity of the ambient air. At 90% RH, a weight gain approaching 2% may be measured but at normal RH (20-60%), the equilibrium water content has been given as 0.2%-0.6% and between 80 and 90% RH it is 1.0-1.5%. This moisture problem accounts for the deterioration of the powder and sometimes of its container under unfavorable conditions. Replacement of charcoal by a purer, non-cellular carbon made from sucrose (sugar) is the subject of U.S. patent 2,415,848, issued to W. H. Rinkenbach and V. C. Allison in 1948. Powders made with such carbon are slower burning than regular black powders.

There has been much speculation about the reactions that take place when black powder burns. Undoubtedly, the products vary with conditions of the reaction, *i.e.*, temperature and pressure. In one older investigation, it was found that 56% solid residue, 43% gas, and about 1% water were obtained. The solids were predominantly potassium carbonate (K_2CO_3), 61%, potassium sulfate (K_2SO_4), 15%, and potassium sulfide (K_2S), 14.5%. The latter might actually be K_2S_2, since the analysis gave also 9% sulfur and several minor products. The gases were carbon dioxide 49%, carbon monoxide 12.5%, and nitrogen 33%, with some hydrogen sulfide, methane, and hydrogen.

The variability of its reactions (aside from variations in composition) has been reviewed by this author in a recent publication[201]. Further information on black powder is given in Chapter 16.

The heat of combustion, assuming all combustion products to be the highest normally-stable oxides, has been given as 1425 cal/g.

By older standards, black powder has very good heat stability. Its explosion or self-ignition temperature has been reported as vary from 180° C to 266° C, but some lower and higher data exist, depending on the method of testing. These figures do not apply to sodium nitrate powder with higher self-ignition temperature, described below.

The sensitivity to impact is low, friction sensitivity very small, but sensitivity to ignition by flame, high. Being a "low" explosive, its brisance as measured by the sand test is only 8 g as crushed sand *versus* 48 g for TNT.

By substituting sodium nitrate for potassium nitrate, a slower burning, somewhat more hygroscopic, less powerful black powder is obtained. Once called "B Blasting Powder," it was used mostly in the form of large compressed pellets for shooting coal in underground mining, clay, and shale.

Historically, the next category of propellant to be developed was the nitrocellulose powders. These are high in gas, low in residue, and adaptable by formula and geometry to a wide range of burning rates and pre-determinable burning-rate variations in the course of their deflagration. In a special group, certain additives make the burning rate nearly independent of the pressure (plateau or mesa burning), but this property pertains only to a limited pressure range. Heat resistance is only fair, and all NC powders tend to gradual, self-accelerating decomposition, especially at elevated temperatures. This, however, can be counteracted up to a point by stabilizing additives.

When cellulose, such as cotton fiber, is nitrated, between two and three nitrate groups enter the basic $C_6H_{10}O_5$ group causing between 11 and 14% nitrogen (N) to enter the molecule. The lowest nitration with 11% N leads to products that are soluble in numerous solvents. As pyroxylin or collodion cotton, they are part of lacquers and plastics, the best-known being celluloid. Not suitable as a propellant, such material is sometimes of pyrotechnic interest as a binder or as a consumable structural component that requires very little oxygen for combustion.

Pyrocellulose and guncotton are more highly nitrated, pyrochemically valuable types of nitrocellulose with 12.6 and 13.35% N, respectively. Pyrocellulose is still soluble in ether/alcohol mixtures, while guncotton has more limited solubility. The two are often blended with each other. Wet extruded, with small additions of nitrates and stabilizers, they form the *single-base powders*.

By colloiding guncotton with nitroglycerine (glyceryl trinitrate), the *double-base powders* are obtained. It is possible to process and extrude these without the use of volatile solvents. This permits the manufacture of large grains without the need for time-consuming removal of solvent and the disadvantage of ensuing shrinkage. Such a propellant is first converted into "carpet roll" (0.080-in. thick rolled-up sheets resembling thin rubber mats) and then is extruded in large, powerful hydraulic presses located in armored bays. "Ball powder" is prepared quite differently, starting from a lacquer-type solution and converting it into tiny spheres by agitation in an aqueous solution of a colloid. The process is applicable both to single- and double-base propellants.

The ratio of nitrocellulose (NC) to nitroglycerine (NG) in double-base powders varies widely and, with it, the energy and behavior of the propellant. The double-base propellants M5, M2, M26 and M9 – all found in PADs – contain 15, 20, 25 and 40% NG, respectively. They are solvent-extruded with the exception of M9, which consists of small flakes.

No smokeless powder currently manufactured contains as much nitroglycerine as did Cordite, with 58%. This once widely used military and sporting powder ceased to be manufactured in the 1960s. "Bullseye®," introduced by Laflin & Rand in 1898, and now manufactured by Alliant (formerly the Hercules Powder Co.), is at present the highest NG-content commercial powder, with approximately 40% NG. High NG content in double-base powders contributes to erosion of the bores of firearms in which the powder is used; the majority of sporting powders have much lower content, *viz.*, 15 to 25%.

Any solid body of propellant will furnish a decreasing amount of gas per unit time when the surface area becomes smaller during combustion at constant burning rate. In order to keep gas evolution constant or even increasing, geometrical, physical, or chemical means are employed. Perforations in cylindrical grains with simultaneous external and internal burning cause the inner surface or surfaces to increase while the outer decreases. The result is production of a more or less constant volume of gas over time. If an external surface is completely prevented from ignition, then the increase of the internal one causes progressive burning, *i.e.*, gas development at an increasing rate. The physical means of such restriction of burning is called inhibition and is done by potting, wrapping, or plastic coating of the surface. If the conditions of removal of the gases are such that the pressure in the chamber or "motor" rises throughout the burning phase, then conditions for acceleration of gas-formation rates may occur independently from the geometry of the powder grain or grains. However, the addition of 2-5% of organic lead salts, such as the salicylate or acetylsalicylate, to double-base propellants has the curious effect of making the burning rate independent of pressure within a limited range, a phenomenon called *mesa* or *plateau* burning because of the appearance of the pressure/burning-rate curve. Ball powder can be surface treated in order to counteract the regressive burning of the spheres. The burning rates of NC propellants are somewhat difficult to compare with ordinary pyrotechnic rates, since NC powders perform poorly at atmospheric pressures and their burning rate is generally represented in a graph of burning rate *vs.* pressures – about 750 kg/cm^2 for regular NC powders and about 75 kg/cm^2 for specially phlegmatized, slow burning mixtures. The latter have burning rates below 0.5 cm/s, while those of the regular NC powders, both single- and double-base, range from 0.5 to 1.125 cm/s.

Nitrocellulose varies in heat of explosion from 734 cal/g for collodion cotton to 1160 cal/g for a high-nitrogen NC with 14.14% nitrogen, but its heat of combustion in air declines with increasing nitration from 2606 cal/g for dinitro- to 2179 cal/g for trinitrocellulose, calculated from

$$\text{Heat of Combustion (constant pressure } 30^\circ\text{ C)} = -4176.7 + 141.26\,N \text{ cal/g}$$

where N is the percentage of nitrogen and the minus sign expresses exothermic reaction.

While all types of nitrocellulose are thermochemically underbalanced in oxygen, furnishing CO, CO_2, H_2O, H_2, and N_2 as products, nitroglycerine is overbalanced and yields CO_2, H_2O, N_2, and O_2. Since the heat of explosion of NG is 1486 cal/g, double-base propellants profit not only from the higher heat of explosion of NG, but also from the reaction of the NC with the excess oxygen. Gas volume (water as gas) for both types varies from 900 to 1000 ml/g at Standard Temperature and Pressure. Both single- and double-base propellants will survive temperatures of 129° C, but such exposure is only recommended for very short periods. The self-ignition temperatures (within 5 seconds of exposure) for pyrocellulose, guncotton, and nitroglycerine have been given as 170° to 230° C.

The high-nitrogen propellants comprise mixtures based mainly on ammonium nitrate, guanidine nitrate, nitroguanidine, and some more unusual gas-formers such as nonexplosive azides, dicyandiamide, 5-amino-tetrazole, and others. This group has the highest gas output, leaves little or no residue, and often furnishes "cool" gas at slow rates.

The decomposition of ammonium nitrate by itself is only a moderately exothermic reaction according to the equation:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O + 8.8 \text{ kcal (exothermic)}$$

With an output of 110 cal/g, it is not initiable from ambient temperature and is barely self-sustaining at elevated temperature; therefore, pyrotechnically it is of no interest. While it produces a physiologically interesting and useful gas ("laughing gas"), the reaction is not free from side reactions in which not only harmless nitrogen but also undesirable higher oxides of nitrogen appear. Eight modes of decomposition have been postulated[234]. These are mostly much more exothermic than the reaction leading to N_2O, furnishing from 219 to 292 cal/g. The same reactions prevail when certain catalysts are added, and in the presence of fuels considerably more heat is evolved. Taylor and Sillitto[235] describe mixtures of ammonium nitrate with 2% charcoal or 12% starch that yield 878 and 860 cal/g and 909 and 938 ml gas/g respectively, calculated at constant pressure and with water considered as a gas. By using cool-burning or hotter fuels, a wide range of flame temperatures can be achieved, from 360 to 2000° C, with gas volumes up to 1350 ml/g. Among fuels mentioned that are also high gas formers are ammonium oxalate monohydrate, $(NH_4)_2\,C_2O_4 \cdot H_2O$, and nitroguanidine.

Ammonium dichromate can act as a catalyst for cool-burning mixtures, some of which can be cast because they melt below 120° C.

Two disadvantages of ammonium nitrate are its hygroscopicity and a crystal-structure change that increases its volume by 3.8% at the unfortunate transition temperature of 32° C, which is the common summer temperature of 90° F over most of the United States. This transition point can be shifted, *i.e.*, depressed by about 20°, but not eliminated, by admixture of 8% of potassium nitrate.

While ammonium nitrate furnishes the slowest burning propellant-type mixtures, the use of catalysts and fuels increases the burning rate to 0.5 to 1.3 cm/s at a pressure of 100 kg/cm². Guanidine nitrate and nitroguanidine are both exothermically decomposing materials of similar reactivity and similarly catalyzed decomposition reactions, without some of the disadvantages of ammonium nitrate, though they are less available and of much higher cost. Gas volumes on decomposition, by themselves or with admixture of ammonium nitrate or various fuels, are also in the same range, about 1000 ml/g. Disclosures by Taylor and Hutchison[236] give examples of these types of propellant. Burning-rate catalysts or "sensitizers" claimed are vanadium oxide (V_2O_5), cuprous chloride (Cu_2Cl_2), molybdic acid, ceric oxide, and others. The burning rates are generally slow at

0.1-0.17 cm/s. Nitroguanidine produces hotter gases and presumably higher burning rates (under comparable conditions) than guanidine nitrate. But in general these compositions are chosen because of their nonviolent reactions and relatively cool gas formation, which makes them useful in turbo starters for aircraft and for dissemination of pesticides.

A final matter is composite and high-temperature-stable propellants. They will probably be needed more and more for supersonic aircraft and space missiles, which develop high skin temperatures or encounter extreme environmental conditions.

Composite propellants, *i.e.,* mixtures of oxidizer salts with various plastic binders (generally about 25% of the latter), have been touched upon above in connection with ammonium nitrate. Plastic binders are pyrochemically quite inert until pyrogenic breakdown occurs at very high temperatures; the most temperature-stable should be the fluorinated polymers. The stability and temperature resistance will then hinge on the properties of the oxidant. From this viewpoint, composite propellants using potassium perchlorate should have the best properties. The conventional ammonium perchlorate composites will in general withstand 150° C for days and 200° C for hours, while the corresponding figures for potassium perchlorate are 50° C higher. A mixture of sodium nitrate, sulfur, and rubber, vulcanized by heating, has been patented as a "composite explosive" suitable to replace black powder, and might possibly be a heat-resistant gas former.

Mixtures of potassium perchlorate and Hycar (acrylonitrile copolymers) not only have good temperature stability but seem not to form toxic gases on prolonged storage. Epoxy resins also have suitable physical properties, but silicone resins have proven disappointing. One must always consider that PADs are often small devices and their propellants should be available as easily handled extruded shapes if at all possible.

In connection with high temperature resistance, attention has been given to actual explosives. As a rule, the so-called high explosives will deflagrate without destructive brisance upon ordinary ignition if not extremely confined or burning in large amounts. However, they are generally much less heat-resistant than azides and styphnates. Exceptions are HMX, trinitrobenzene (TNB), and Hi-Temp, a proprietary material based on RDX.

Commercially available is the explosive Tacot[31] of melting point 378° C, at which point it decomposes rapidly, while claimed to be stable below that temperature. Under development in government laboratories are compounds that in combination with certain plastic binders have cook-off temperatures up to 550° C.

Chapter 23
Glossary

The following glossary is modeled on that used by the late Herbert Ellern in *Military and Civilian Pyrotechnics*. The bulk of his material has been retained; most of the additions relate to fireworks. Some of Dr. Ellern's introductory remarks are even more pertinent now than when first published in 1968:

> Style comes out of love for the written word, which is nurtured by copiously reading well-written and preferably nonscientific literature. It is marred by grammatical illiteracies (*this* data, *this* phenomena) even though these may parade as "modern usage." Furthermore, the unusual and special word has its place in a special field of knowledge and its use is not an unnecessary show of learnedness or deliberate obscurity....
>
> The glossary that follows is a collection of words appearing in the text (and a few not occurring there) that may be unfamiliar to some readers and also to otherwise competent and scientifically schooled secretaries... The author has been guided by his own preferences, aiming at the pitfalls rather than at comprehensiveness.

ablation:	the wearing away of a surface material by hot gases, resulting in protection of the material (such as a nose cone) below it
absorption:	the act of "soaking up" and retaining a gas in a liquid or a liquid in a solid; also, retention of radiant energy
accelerating rate calorimetry (ARC):	a technique of studying the kinetics of an exothermic reaction by measuring the rate of temperature increase of a sample confined in a heated adiabatic pressure vessel
accuracy:	closeness to true value; not to be used indiscriminately as a synonym for *precision*, which means reproducibility of measurement

actuator (explosive):	a self-contained power transmitting device which converts chemical energy into mechanical force. Removers (retractors), thrusters, dimple motors and similar devices fall into this category.
additive:	a substance added to a basic composition to accomplish some specific result. Typical additives include binders, catalysts and spark-producing metal powders.
adiabatic:	occurring without gain or loss of heat
adsorption:	taking up of a gas or liquid by a solid due to surface energy. Compare a*b*sorption.
ærosol:	a system of extremely fine droplets or solid particles in a gas (usually air); popularly, a cloud of relatively coarse liquid droplets from a pressurized spray can
ambient:	surrounding on all sides; used mainly for the existing "normal" conditions of temperature and pressure in a terrestrial environment. Its use implies (if not stated otherwise) that the object itself has reached the ambient condition.
amine:	an organic compound containing the $-NH_2$ group, such as ethylenediamine
ammine:	a part of an inorganic coördination compound containing the NH_3 molecule, such as tetrammine copper (II) chlorate
amorce:	a toy cap of the type used in cap pistols. This term is derived from the French and is mainly seen in Europe.
anode:	in electrolysis or electroplating, the positive electrode toward which the negative ions move. In a storage battery or a cell which is generating current, the negative terminal is called the anode.
atomizing:	refers to the conversion of molten metal, by a blast of air or inert gases, into tiny spheroidal droplets which form a powder on solidification
attenuate:	generally, to weaken, reduce or mitigate. In electronics the term has a specialized meaning.

autoöxidation:	fairly rapid combination with atmospheric oxygen under ambient conditions
auxiliary:	thus, although frequently misspelt "-ll-"
average:	strangely derived from the French word *avarie* or shipwreck, indicating the early relation of statistics to insurance underwriters. In modern statistics the term "mean" is preferred.
ballistics:	the study of the motion of projectiles. "Internal ballistics" refers to phenomena which occur within the bore of a weapon; "external ballistics," to those occurring after the projectile is in free flight.
bandoleer:	a belt having loops or pockets to hold small-arms ammunition or similar items, to be worn over the shoulder
batch:	see *lot*
Belleville spring:	a curved, resilient piece of steel or plastic, usually circular, sometimes with a center hole. It is used as a spring tension washer, or, arranged to flip over, as the driving force on the percussion primer of an antipersonnel mine or for other similar purposes.
Bickford:	after William Bickford (1774-1834), of Tuckingmill, Co. Cornwall, England, its inventor – a type of pyrotechnic delay fuse consisting of a core of specially-formulated black powder around which is spun textile fibers, over which in turn may be further layers of textile (called countering), coatings of asphalt, gutta-percha, lacquer, or outer wrappings of cloth tape. Compare *safety fuse*. Not to be confused with Primacord-Bickford, Ignitacord-Bickford, Cordeau-Bickford, and other blasting-related products manufactured by companies established by, or licensed to use the name of, Bickford.
billion:	represents the magnitude of 10^9 in the United States but 10^{12} in many other countries, and for this reason should be avoided in scientific terminology
black body:	an idealized concept of a solid radiating substance

black powder:	generally, a mixture of potassium nitrate, charcoal and sulfur. A very intimate mixture in a ratio of approximately 75/15/10 or 6/1/1 is the most energetic, and is the type implied when the term *gunpowder* is used. Other mixtures, in different ratios or not as well incorporated, are used for a wide variety of purposes. Variants which lack sulfur, or which contain sodium nitrate, may also be considered black powder but the difference is usually specified.
black shell, *also* **blind shell:**	a firework shell which leaves the mortar but fails to burst in the air
blasting cap:	a small metal tube containing a primary explosive that detonates from an electric bridgewire or from safety fuse, for the purpose of initiating a high explosive
blasting powder:	a term properly applied to industrial grades of milled and granulated black powder, as opposed to sporting or military grades. Today black powder is hardly used in commercial blasting operations, although it is still preferred for quarrying some kinds of stone. The term "blasting powder" is often loosely applied to commercial high explosives as well. Also, before dynamite and similar agents became common, there were various proprietary mining powders, some of which contained chlorates, barium nitrate or other oxidizers. In reading old accounts one should not always assume that black powder was being used.
bombette:	a miniature fireworks bombshell used inside a larger device, especially in a Roman candle
booby trap:	a concealed antipersonnel explosive charge, set off unexpectedly by such means as a trip wire, pressure, or the opening of a door. If concealed underground and actuated by being stepped on, the device is called an antipersonnel *mine*.
bottom shot:	a final heavy report in a cylindrical firework shell
bouchon:	(French, *cork, stopper*) a closure in a grenade or similar device, hence, *bouchon fuze*, a pressure release type fuze installed on a hand grenade

bounce:	a mild report charge, typically black powder, placed in the end of a tubular firework such as a serpent or fountain
braze (brazed, brazing):	to solder with a nonferrous metal that melts at a lower temperature than that of the metals being joined. One often sees this spelled "braise", something which should not be done to gun parts or other ordnance materials, as they hardly ever become tender enough to eat.
bridgewire:	a resistance wire incorporated into an ignition element attached to the leads of an electric igniter or electro-explosive device
brisance:	the shattering effect of an explosive - adjective, *brisant*
Bruceton test:	a method of sensitivity testing to estimate the mean and standard deviation from a limited number of samples, also called the "up and down" method. The testing is carried out at evenly spaced levels around the mean.
burning rate:	usually measured in inches per second, m/sec, mm/sec or similar units. The inverse, *i.e.*, sec/in, or the total burning time, should not be called burning *rate*.
cake:	(fireworks) a battery device which consists of multiple tube items (such as fountains and small mortars) made into a bundle and intended to be sold as a unit
calorimeter:	a device for measuring heat of combustion (under compressed oxygen or with sodium peroxide), or heat of explosion (under an inert gas such as argon). The latter is used for propellants, explosives and pyrotechnic mixtures, which react without outside oxygen. A c*o*lorimeter is a machine which measures color, usually absorption at a specific wavelength.
canister:	a metal can for hand-thrown chemical munitions, typically about the size of a beer can; often misspelt "cannister"
cannonade:	in fireworks, an ærial device which produces multiple loud explosions, generally without precise intervals between them

catalyst:	strictly, a substance that promotes a chemical reaction but is not changed in the process. More broadly, the term is applied to almost any substance used in relatively small amounts to promote a reaction.
cathode:	the electrode at which reduction takes place, by convention deemed to be negative
celebration string:	a roll of Chinese firecrackers, usually of different sizes, designed to be unrolled and suspended before igniting
chain:	a group of firework items, such as shells, exploding devices, or waterfall cases, connected by piped match
chalcogen:	an element in the oxygen family, *i.e.*, sulfur, selenium or tellurium
chemiluminescence:	light emission from a chemical reaction, not ascribable to incandescence (*q.v.*). This phenomenon produces little or no heat and is commonly called "cold light."
choke:	a constriction in a case charged with pyrotechnic composition. It may be made by "pulling in" the paper case while still damp from rolling, by pressing a clay washer in it, or by crimping a metal washer in place. Chokes are used in many types of rockets (where they are sometimes, incorrectly, referred to as *venturis*) and also in *gerbs* (*q.v.*).
chrysanthemum:	a spherical firework shell which produces a globular pattern of tailed stars. A similar shell in which the stars do not leave tails is called a *peony*. The general Japanese term for hard-breaking ball shells of this type is *warimono* (*q.v.*).
cigarette-type burning:	a linear progression of the flame or glow front in a column of solid reactants
classification:	arranging information into groups of restricted availability with the intention of safeguarding national security. In ascending order of severity, the present U.S. labels are: *confidential, secret, top secret*. Formerly the lowest level was "restricted," but this term no longer has official status.

comet *or* **comet star:**	a cylindrical pellet of streamer composition, used in many firework applications and occasionally in military signalling pistols
comminute:	to pulverize, triturate or break up into small particles
compatibility:	absence of unwanted interaction of the components in chemical mixtures, either with each other or with adjacent materials (NOT “-ability”)
composite propellant:	a solid propellant that contains an inorganic oxidizer salt plus a plastic binder, which also serves as a fuel
composition:	broadly, any pyrotechnic or explosive mixture, as opposed to a discrete chemical compound such as TNT. In the military the term is especially applied to a castable or moldable explosive containing more than one ingredient, such as “Composition B” or “Composition C-4.”
cordite:	an obsolete double-base smokeless propellant, which was extruded in the form of long strands. It was developed by the British government in 1889 for the .303 service rifle, and was also extensively used in a family of powerful sporting rifles known by the term “nitro express.” Coarser varieties of cordite were employed in cannon. The original version contained 58% nitroglycerine, and although very powerful, it was also very erosive to rifle bores. Cordite has not been manufactured since the 1960s. Unfortunately the word holds a fascination for popular writers, who misapply it to almost any “nitro” or “smokeless” powder. To complicate matters there was also a “revolver cordite,” chopped into short pieces, which bears a physical resemblance to some modern single-base powders.
crackle:	a firework effect produced by embedding small explosive granules in a matrix of black-powder-based composition, as in a fountain or a comet star. The granules typically contain magnalium and a metal oxide. Coarsely ground magnesium/aluminum alloy alone may also produce a crackling or sizzling sound, but it is not as loud. Different crackling preparations may be used for the cores of round stars.

critical material:	something which may not be available in sufficient quantity in the event of war
crossette:	a firework *comet* (*q.v.*) which contains a small explosive charge to make it split into several pieces at mid-trajectory
deflagration:	the rapid burning of a compound or mixture without detonation (*q.v.*). Some confusion exists regarding the use of the word deflagration to characterize non-detonating explosives. It might be preferable to restrict the term to fast exothermic reactions that are not regarded as explosions, but in practice, "deflagration" is used for both.
delay:	a device for timing sequences of events. Besides being purely pyrotechnic, delays may be mechanical, electronic or physico-chemical.
deliquescent:	tending to liquefy; specifically refers to very hygroscopic materials which attract enough moisture from the air to be at least partially dissolved
demil (to):	(from *demilitarize*) to break down outdated, obsolete, or surplus munitions to their components, which then may be recycled or otherwise disposed of in an appropriate manner
destruct system, *also*, **to destruct:**	modern "back-formations" from the word destruction, signifying the means to destroy a military item in order to render it harmless, or useless to an enemy
detent:	a device that locks and unlocks a mechanism, such as the flip-over lever on certain booby trap release designs. The "safety" on an ordinary hammerless firearm is also a type of detent.
deterrent:	a surface treatment for a solid propellant, which reduces initial burning rate – essentially a synonym for "inhibitor"
detonation:	a type of explosion of the highest rate of propagation, accompanied by a shock wave. It is often defined as a

	rate of propagation which exceeds the speed of sound in the same material. The word detonation should not be used indiscriminately: a deafening "bang" does not signify detonation merely because of its loudness. Detonation is also called "high-order" explosion, in contrast to "low-order" explosion produced by mere expansion (as occurs with black powder).
detonator:	a more general term than *blasting cap* (*q.v.*) for an explosive initiating device, which in turn may be initiated by a primer, fuse or other source of heat input
diatomaceous earth:	a rather bulky natural material consisting of the silica "skeletons" of tiny marine organisms; also called *infusorial earth* and (rarely) *diatomite*. *Fuller's earth* and *bentonite* have somewhat similar properties, but are chemically types of clay.
diluent:	an inert or nearly inert substance, used to add volume or to reduce the rate of a reaction. In dry pyrotechnic mixtures, typical diluents include silica and sawdust. In liquids such as lacquer or binding solutions, a diluent may be a liquid which is compatible with the solution but has poor solvent properties by itself.
discreet/discrete:	One should use discretion in keeping the meanings straight, as in "*discrete* oxidizer particles," but "be *discreet* in talking to strangers about military pyrotechnics."
double-base propellant:	a propellant containing two active ingredients, specifically nitrocellulose and nitroglycerine. There are also single- and triple-base propellants.
draw-out shell:	a cylindrical firework shell which contains four timed reports, with or without stars, in the first break; this is followed by another full-sized shell break and finally a heavy report
drift signal:	see *float signal.*
driver:	a tubular device containing rammed composition, used to impart motion to a fireworks piece such as a wheel

DTA/DDTA:	*differential thermal analysis*; *derivative differential thermal analysis*: test methods, both of which involve gradual heating, for pyrotechnic mixtures
dummy:	a nonexplosive item resembling a round of ammunition, a bomb or the like, designed for demonstration, camouflage, or training. It differs from an *inert* munition, which is an actual, potentially usable item that does not currently contain any "live" materials.
electric match:	a device for the electric actuation of pyrotechnic or explosive articles, consisting of a small quantity of composition, electric leads, and usually a "bridgewire" of high resistance, which is raised to sufficient temperature to ignite the composition by the passage of an electric current through it. "Non-bridgewire" electric matches, relying on the partial conductivity of the pyrotechnic composition used, are also made. Electric matches are components in a variety of electric initiation devices, such as electric blasting caps and electric squibs. Colloquially, electric matches are themselves sometimes called squibs; but a true electric squib contains pyrotechnic composition in addition to that of the match head. Compare *squib.*
endothermic:	proceeding with absorption of heat
enthalpy:	in thermodynamics, a term meaning total heat energy
entropy:	an index of the degree to which the total energy of a thermodynamic system is uniformly distributed and is thus unavailable for conversion into work
envelope:	a casing or container, specifically, a thin one like those used in flares
environmental testing:	refers to the exposure of military items to climatic, mechanical and other external stresses – does not necessarily imply testing for toxic pollutants or other adverse effects

éprouvette:	among the earliest quantitive measurement tools in pyrotechnics, éprouvettes were introduced as early as the sixteenth century for testing the strength of black powder. Several forms exist, *e.g.*, those of Furttenbach and of Saint-Rémy; usually the term denotes a black powder tester, but it may also be applied to devices for testing other explosives, *e.g.*, Nobel's mortar.[72]
equation of state (EOS):	the relationship between variables of state in a thermodynamic system, *i.e.* pressure, density, and temperature
error:	in statistics, not the same as a mistake: *error* pertains to deviation from a true value, and may be unavoidable
eutectic:	of the possible mixtures of given substances, the one having the lowest melting point
exothermic:	occuring with release of heat; of compounds, having been formed from the elements with release of heat
exploding bridgewire:	a bridgewire functioned by a high-energy capacitative discharge, capable of initiating secondary explosives or pyrotechnics without the need for a primary explosive or igniter
explosive switch:	a small self-contained, electrically intiated device that causes one or more electric circuits to be opened and/or closed by "explosive" or propulsive action
feasibility study:	a much misused and over-used term which denotes the determination of the practicability or advisability of a device or technique for an intended purpose
field expedient:	a material or device, usually an explosive or other weapon, that can be made by simple means from readily available substances, especially behind enemy lines or in guerilla warfare
firecracker:	a fireworks device consisting of a paper case containing an exploding mixture and a fuse to ignite the same, designed to produce a single loud "bang" without other effect; compare *salute, report*. "Crackers" do not always mean firecrackers of this type; in British references, they

	often signify a type of long paper tube, filled with fine-grained blackpowder and folded in a zig-zag pattern, intended to produce a series of mild reports. "Firecrackers" is a term often vulgarly used to encompass all fireworks. This usage is to be discouraged.
first fire:	a pyrotechnic composition used to propagate fire to a more difficult-to-ignite composition; similar to, but not the same, as a *prime* (*q.v.*)
flash powder:	a pyrotechnic composition, usually containing aluminum or magnesium (but also occasionally titanium, zirconium, or other more exotic metals) used to produce a bright flash for illumination of a photographic subject (compare *photoflash*) or in fireworks, for a flash-and-sound effect
flechette:	a dart or small fin-stabilized missile, usually intended to be fired from small arms or dispersed by explosive
flight:	(noun) in fireworks, a group of similar devices (such as rockets) fired simultaneously; a volley
flitter:	**1:** a type of coarse flake aluminum; individual flakes are large and visible to the naked eye, *e.g.*, 30-80 mesh is considered a "fine flitter," 12-40 mesh a "coarse flitter." **2:** a firework effect characterized by combustion which forms a glowing semi-reacted dross; this semi-reacted dross, as it falls through or is propelled through the air, reacts to completeness, emitting flashes. *Flitter* is the American term for this effect, *glitter* the corresponding British usage (though widely adopted in the United States in recent years). Compare *glitter*, *tremalon*. **3:** erroneously, a firework effect made with a composition containing aluminum flitters; a tailed star with a metal fuel.
float signal:	a light- and smoke-producing day and night marker, which can be dropped from aircraft as a reference point
flower pot:	(in fireworks) **1:** a traditional kind of fountain, which contains lampblack and produces a distinctive form of sparks known as "spur fire;" **2:** the upward spray of stars and other burning material produced when an ærial shell explodes in its mortar

fluorine:	a candidate for top honors in a misspelling contest, along with derivative words such as *fluoride* and *fluorocarbon.*
formula:	**1:** a prescription; a recipe (*Webster's*). **2:** an expression for the chemical composition or constitution of a substance, using the standard notation introduced by Berzelius and later modified; as, for example, the formula of potassium chlorate, $KClO_3$
formulation:	the act or result of formulating (*Webster's*). Since to formulate is to reduce to, or express in, a formula, a recipe can be among the results of formulating. Recently, the fashion has arisen of referring to a recipe as a formulation, and of confining the use of *formula* to the second sense defined above. This pedantry has no basis in sound English usage and is to be discouraged on the principle of parsimony.
frangible:	tending to break up into powder or small fragments; brittle. Some materials of this type are relatively strong, as opposed to those considered *friable.*
fulminate:	strictly, a salt of fulminic acid ($HONC$), sometimes called paracyanic acid. More broadly, especially in older literature, the term is applied to almost any easily detonated material and is essentially a synonym for *primary explosive.*
functioning time:	the elapsed time between application of initiating energy and the desired effect
fuse:	an ignition device in the form of a cord or tube that contains a pyrochemical mixture. Specific types include safety fuse, quickmatch, and the twisted tissue paper fuse found in Chinese firecrackers.
fusee:	a warning flare; also, a special variety of match, the head of which has a long burning time and is difficult to extinguish
fuze:	an igniting or detonating device, particularly in a military shell, bomb or torpedo. Use of this spelling implies a mechanical or electrical component, rather than a purely pyrotechnic delay (compare *fuse*).

gage:	an accepted variant of *gauge* - "guage" is never correct.
garniture:	device carried by an ærial firework such as a shell or rocket. Common garnitures include stars, whistles, hummers and reports.
gasless:	denotes a pyrotechnic mixture that reacts with the release of minimal amounts of volatile matter; few if any are truly gasless
gerb:	(French, *wheat-sheaf*) A firework consisting of a choked paper tube charged with a spark-producing composition, designed to be fixed to the framework of a set-piece to produce a spray of sparks. Also sometimes spelled *gerbe.*
girandola:	A fireworks wheel intended to be fired in an horizontal position, with drivers so positioned to provide both rotation and lift, so that the wheel rises from its firing position into the air; it may rise and fall with several succeeding groups of drivers, and may conclude with a discharge of stars or garnitures. *Girande* is often seen in French works with another meaning, namely a flight of rockets at the end of a display.
glitter :	a firework effect characterized by combustion which forms a glowing semi-reacted dross; this semi-reacted dross, as it falls or is propelled through the air, reacts to completeness, emitting flashes. Primarily a British usage, though increasingly current in the United States. See *flitter*, def. 2., and *tremalon.*
grain:	**1:** a unit of weight which is the same in the avoirdupois, apothecaries' and troy systems of measurement, equivalent to 64.8 milligrams **2:** (in rocketry) a single piece of solid propellant, regardless of size
grain powder:	black powder which has been formed into hard granules - for all practical purposes, synonymous with *gunpowder*
gram:	Unfortunately, different abbreviations are in use for this basic metric unit of mass: *g* is most frequently used, but also *g.*, *gm* and *Gm.* One that should NEVER be used is *gr*, the correct abbreviation for *grain.*

grenade:	a small explosive, pyrotechnic or chemical missile, either thrown by hand or propelled from a special launcher, such as an adapter unit attached to a rifle
gum:	the generic name given to a group of amorphous carbohydrates having the general formula $(C_6H_{10}O_5)_n$, occurring in almost all plants. They are entirely soluble or soften in water, forming with it a thick glutinous liquid or mucilage. The term is often incorrectly or colloquially applied to resins, as in "red gum," "gum rosin," or oleo-resins, as in "gum turpentine," etc. The problem is compounded by the existence of gum-resins, in which water-soluble carbohydrates are naturally mixed with true resins, and by oleo-gum-resins, in which these components are present together with an organic solvent or volatile oil. Compare *resin*.
guncotton:	a high-grade nitrocellulose containing 13% or more of nitrogen, insoluble in ether-alcohol but soluble in acetone and in ethyl acetate
gunpowder:	strictly, an intimate mixture of potassium nitrate, charcoal and sulfur, which has been milled and granulated to maximize performance. Compare *black powder*. In modern times the term has been broadly applied to smokeless propellants as well. However, the simple word *gunpowder* implies the original black, especially in Great Britain and Commonwealth countries. In this context "meal-" or "mealed gunpowder" is valid, even though it is poorly suited for propelling shot, because commercial meal powder has been through the same manufacturing processes. Likewise, although it is not intended for firearms, "sulfurless gunpowder" has been milled, pressed and crushed. Black powder variants which have been mixed by simpler methods burn much more slowly than true gunpowder.
hammer shell:	an ærial shell which releases smaller color shells and reports, timed to explode alternately. Instead of color breaks, a hammer shell may contain two different kinds of reports, such as flash and dark reports, or colored flash.
hangfire:	unintended delay in the ignition of a munition or pyrotechnic device, usually followed by normal performance

hermetic:	airtight, also, impervious to other gases
high explosive:	a material capable of true detonation (*q.v.*). High explosives are based on the dissociation of chemical compounds such as organic nitrates, aromatic nitro compounds, or nitroamines, rather than the combustion of inorganic oxidizers with fuels. Some explosives contain all three types of ingredients, and one component may serve more than one rôle.
howitzer:	a weapon that fires its projectile with more velocity than a mortar, but lower velocity than a full-length cannon of the same caliber. Typically a howitzer is fired at greater elevation than a cannon, but at less elevation than a mortar.
Hugoniot:	also called the Rankine-Hugoniot equation, relates the change of energy across a shock front to the equation of state of the material. The EOS of shocked material is tabulated in the literature[62, 119, 156].
hydrophilic:	having a strong affinity for water, swelling or dissolving in it (opposites: *hydrophobic*, also *lipophilic*)
hygroscopic:	readily absorbing water, especially from the atmosphere (not "hy*d*roscopic")
hypergolic:	refers to a propellant combination that ignites spontaneously when the fuel contacts the oxidizer. This word is derived from a German World War II code word, "gola." The noun *hypergol* is occasionally seen. Similar coinages such as "propergol," "monergol," "katergol" and "lithergol" are used in Germany, but rarely in English-speaking countries.
Iditol:	trade name for a Russian synthetic resin of the novolac (*q.v.*) type, mentioned by Shidlovskii[214]. It should not be confused with *iditol*, a common or trivial name for 1, 2, 3, 4, 5, 6-hexanehexol.
igniter:	usually refers to an ignition device which is electrically initiated (not "ignitor")
illuminant:	a pyrotechnic mixture specifically formulated to produce light

implosion:	the opposite of explosion; an inward burst of particles, gases, etc. due to reduced pressure or from a surrounding explosive
impulse:	the stress imparted to a system, integrated over time, as in drop-hammer tests. The term is also applied to the force exerted by a rocket motor, integrated over time (see *specific impulse*)
incandescence:	light emission from a substance due to its high temperature
incendiary:	a material used for destructive ignition
initiator:	the first element of an explosive or pyrotechnic train, normally containing a sensitive primary explosive
in situ:	literally, "in place;" in pyrotechnics it refers to a material (such as a gas) produced where it is to be used
intense/intensive:	the latter is often used where the former would be more correct, *e.g.*: *intensive* study but *intense* heat
iso-:	equal; a prefix used in many scientific terms
isobaric:	taking place under constant or equal pressure
isochoric:	obtained under constant volume conditions, as an isochoric flame temperature
isochronal/ isochronous:	synonymous words meaning of equal time
kamuro:	(Japanese) A firework shell intermediate in effect between the *poka* (*q.v.*) type of "willow," and the *warimono* (*q.v.*) or "chrysanthemum." It has the more forceful break of the *warimono*, and tailed stars of long burning duration, like those of the *poka* willow. The effect is to open with the burst radius of a chrysanthemum, but instead of going out, the stars continue burning, producing a drooping pattern, like a parasol or an upside-down bowl. The names "crown chrysanthemum," "crown willow," "diadem chrysanthemum," or "diadem willow" all have been used to describe this shell in English-language importers' lists. In the United States, the word

	is often used more loosely, to mean any effect, star, or star composition of the willow type.
kraft paper:	paper made by the *sulfate* process (from German, *kraft* or strength); so called because its long fibers give it greater tensile strength than papers made by the sulfite and soda processes. A variety of kraft papers are made, including the brown kraft wrapping paper used in fireworks, papers for bags and envelopes, and (by a modification of the original process) white and other colored papers suitable for printing or writing.
laminac:	proprietary name for a plastic binder material – a polymerizable unsaturated polyester
lance:	a small colored flare used in fireworks displays, especially to make letters or other designs
Langlie test:	a method of sensitivity testing developed in the 1960s to overcome the dependence of the Bruceton method on the choice of step size. The experimenter must specify lower and upper stress limits, the first test being conducted at a level midway between them. Less susceptible to variation in efficiency caused by inaccurate test design, as compared to earlier methods, the Langlie method is most efficient when the upper and lower limits are ±4 standard deviations from the mean.
lanyard:	a strong cord used for firing a device (such as a cannon) from a safe distance
lead oxide:	by the conventions of chemistry, this term specifically refers to the monoxide, PbO, also known as litharge. More commonly used in pyrotechnics is lead tetroxide, Pb_3O_4, known as *red lead* or *minium.* Also occasionally used is lead dioxide, PbO_2, which is sometimes called "lead peroxide."
leader:	a fast fuse that transfers fire down the muzzle of a mortar to a firework shell, or more broadly, to any large piece of fireworks. Except in some small shells sold to the public, leaders are made of piped match (*q.v.*).

loading density:	the weight of pyrotechnic composition or explosive in a device, per unit volume
lot:	a quantity of material or manufactured items produced under identical conditions, as far as possible, but not necessarily in one *batch.* A batch consists of product assumed to be uniform because of the nature of its processing. Several lots (or batches) of powder or the like can be blended to produce a *homogeneous lot.*
machine:	in fireworks, a large elaborate construction, typically a façade of a castle or fort, on which ground pieces are mounted. It may also conceal mortars, people, or mechanical devices.
Mark (Mk):	followed by a number, designates Navy items; an added "Mod" means modifications starting with *zero*, which is pronounced "oh" and means none. A simple *M* signifies ordnance items in general, such as the M-80 firecracker or M-16 rifle.
maroon:	a device which produces a single loud explosion especially in fireworks or signalling: a salute
match:	**1:** a class of cord fuses that includes *slow match* and *quickmatch* (*q.v.*) – used in singular form only. **2:** a strip or splint of combustible material (usually cardboard or wood) tipped with a chemical mixture that bursts into flame when subjected to friction (plural – *matches*).
matériel:	a word used in singular form only, meaning "all kinds of materi*a*ls," usually those supplied by an institution such as the military
medium:	a liquid in which particles are suspended, also called a vehicle
memory:	a material, such as a piece of metal or plastic, is said to have "memory" if it tends to return to the shape or size in which it was cast or molded.
metathetical:	refers to reactions of the type $AB + CD \rightarrow AC + BD$, also called *double decomposition* or *double displacement*

mine:	**1:** an encased explosive designed to destroy enemy personnel, vehicles or ships, usually concealed in water or underground. **2:** a firework which propels multiple burning pieces from a single mortar tube.
missile:	broadly, any weapon that is thrown or projected, but today the term is generally reserved for those which are rocket-powered. In consumer fireworks, the word *missile* is commonly applied to a rocket which has fins instead of a guiding stick.
Misznay-Schardin:	a special type of shaped charge
mock-up:	a model, often crude or improvised, used for training
multibreak *or* **multiple break:**	a cylindrical firework shell containing more than one full-diameter section within a single outer casing. In a true multiple break, the time fuse of each section is ignited by the burst of the previous section.
Munroe charge:	see *shaped charge*
Munroe effect:	the characteristic effect of a shaped charge (*q.v.*)
napalm:	any of several materials that convert combustible liquids such as gasoline to a congealed state. By extension, the resultant gel itself is now called napalm.
nascent:	in the process of "being born," used of a compound or element at the moment it is chemically created, and implying that it is especially active. Chemists, who formerly learned more Latin than is customary now, used to speak of hydrogen *in statu nascendi* – a powerful reducing agent.
Neyer D-Optimal test:	a method of sensitivity testing developed in the late 1980s, designed to extract the maximum amount of statistical information from the test sample. There are three parts to the test: the first designed to "close in" on the region of interest, the second to determine unique estimates of the parameters efficiently, and the third continuously refining the estimates once unique estimates have been established. Unlike earlier methods, this method

	requires detailed computer calculations to determine test levels, and was not practical until computers became widely available in the laboratory.
nitro powder:	a synonym for *smokeless powder*, NOT a high explosive or blasting agent. The term is primarily used in Britain, where firearms must pass either black powder proof or nitro proof. However, the Remington Arms Company also designates some of its ammunition "Nitro Express" or "Nitro Magnum."
Nonel, Nomatch:	"shock tube" for the non-electric almost instantaneous propagation of ignition or detonation to multiple devices. A variety of types exist, some involving a detonation-to-deflagration transition.
novolac:	a thermoplastic resin formed by reaction of phenol with formaldehyde in a ratio greater than 1:1 under acid conditions. Such resins are sometimes used as pyrotechnic fuels. The Russian product *Iditol* (*q.v.*) is an example of the type. Compare *resole*.
obturate:	to obstruct or close, specifically, to seal an item to prevent the escape of gas
ordnance:	military weapons and ammunition; sometimes used to include related equipment such as vehicles and repair tools.
oxalate:	thus spelt, not "oxylate" – a salt of *oxalic acid*, which takes its name from *oxalis*, the Latin name for wood-sorrel
oxygen balance:	in an explosive or pyrotechnic mixture, the percentage excess or deficiency of oxygen as compared with that required to convert all the carbon to carbon dioxide and all the hydrogen to water
PAD:	stands for propellant actuated device; an older term is *CAD* – cartridge actuated device.
palm tree:	a firework shell or rocket burst which deploys only a few large, long-tailed streamer stars. In some old texts on fireworks, the term refers to a ground piece resembling a tree.

passfire:	a quickmatch connection from a time fuse at the top of a firework shell to the lifting charge at the bottom
peony:	a hard-breaking spherical shell of Japanese style in which the main (outer) stars do not have tails (compare *chrysanthemum*, *warimono*).
percussion cap:	a priming device designed to be activated by impact, specifically, a type used with muzzleloading arms, which is placed on a nipple outside the weapon's bore
percussion primer:	a general term for any initiator fired by a blunt firing pin or a hammer, whether it is used in firearms or in other devices such as grenades
permissible:	a type of high explosive that functions with low flame temperature and minimal duration, making it safe in coal mining and other conditions where flammable gas or dust may be present
phlegmatize:	to slow down, to make less active
phosphorus:	(noun) undoubtedly, the most-misspelt word in pyrotechnics. *Phosphorous* is an adjective, often accented on the second syllable, which specifically refers to phosphorus in its lower valence states. Thus, *phosphorous chloride*, *phosphorus trichloride* and *phosphorus (III) chloride* are all correct, but NOT "phosphorous pentasulfide" or "red phosphorous."
photoflash:	Photoflash powder or composition is a pyrotechnic mixture that burns very rapidly, yielding a large amount of light. It normally contains powdered aluminum, magnesium, or an alloy of the two, but may contain other reactive metals such as zirconium. Photoflash cartridges or bombs released from aircraft can illuminate large areas for night photography.
pillbox:	a firework star made by pressing composition into a thin-walled paper tube
piped match:	*quickmatch* (*q.v.*) enclosed in a paper or plastic sleeve. When ignited it burns almost instantaneously, the hot gases from the combustion of the powder being confined within the pipe or sleeve and communicating fire to the entire length with great rapidity.

pistil:	in a spherical firework shell, a central core of small stars, the color of which is contrasting or complementary to the outer stars
poka:	(Japanese) a type of spherical shell characterized by a relatively thinly-papered case and a relatively small burst charge, used to discharge such garnitures as small reports, parachutes, paper figurines for day-time use, and stars that it is desired to deploy without much radial dispersion. Compare *willow.*
polverone:	(Italian, *"big"* or *"coarse" powder*): a type of handmade black powder used in fireworks, coarsely granulated by a wet process. The ingredients approximate ordinary black powder proportions, but may not be exactly 75 potassium nitrate, 15 charcoal, 10 sulfur – and a binder such as dextrin is included. The spelling *pulverone* is also seen.
portfire:	a small pyrotechnic flare, specifically designed for lighting other pieces of fireworks. Portfires are less common now than formerly, though the word is often applied to any flare adopted for this purpose, such as a railroad fusee.
pressure cartridge:	a pyrotechnic device which generates gaseous products under pressure to do mechanical work
primary explosive:	an explosive that can be detonated easily by percussion, heat, or electrical discharge, and is used to initiate other explosives
prime, priming:	the act of preparing a firearm, cartridge, pyrotechnic device, etc., for ignition; also, a sensitive or easily ignited mixture used for this purpose
Probit test:	an early method for estimating the mean and standard deviation from a number of samples. Six is a typical number of test levels and ten or more items are tested at each level. Disadvantages of the Probit method are that large numbers of items have to be tested and test levels have to be chosen properly.[41] Its advantage is that the analysis could be performed with the aid of tables and without difficult calculations, but the advent of computers in the laboratory has largely made this irrelevant.

progressive burning:	Although the term "progressive" covers a multitude of sins, when used with reference to propellants, it means that the surface area increases as combustion proceeds.
propellant:	a pyrotechnic mixture or modified explosive suitable for propelling a projectile such as a bullet, shell or rocket. The word is also spelled *propellent*, with some argument depending on what country one is in, and whether it is used as a noun or an adjective.
pumped star:	a star, almost always cylindrical, which is formed by ramming or pressing composition in a device called a star pump
pupadelle:	a miniature cylindrical star shell used as an insert in larger devices, specifically in a shell-of-shells. Compare *bombette*.
pyrochemical:	relating to or involving chemical activity at high temperatures (*Webster's*). The word is usually, but not always, equivalent to *pyrotechnic*; such reactions also occur in ceramic manufacture and other fields.
Pyronol:	a thermite mixture containing nickel powder which facilitates its ignition; it was specifically designed for underwater use
pyrophoric:	tending to ignite spontaneously on exposure to air. The noun *pyrophorus* is considered archaic and is rarely used today.
quickmatch:	cotton cord impregnated and coated with black powder, used for rapid transfer of fire. It is often encased in paper tubing, causing it to burn almost instantaneously, and is then called *piped match* (*q.v.*).
ram:	to compress a pyrotechnic mixture, especially within a casing, whether by mallet blows or by mechanical pressure
redundant:	usually means superfluous and unnecessary, but in military parlance refers to deliberate multiplication of a single auxiliary device (such as an ignition system) to increase the probability of success

refractory:	highly resistant, especially to high temperature. *Refractive* refers to the bending or deflection of light waves.
regressive burning:	refers to a propellant grain that decreases in surface area as combustion proceeds
repeating shell:	a synonym for *multibreak*
report:	a loud, sharp explosion in a firework or signal device, specifically one at the end of the device's performance
resin:	any of various amorphous, solid or semi-solid organic substances, chiefly of plant origin, sometimes synthetic, and soluble in organic solvents but not in water. Compare *gum. Rosin* is a specific type of resin, derived either from the free-flowing sap of trees of the pine tribe, or by chemical extraction from their woods. All rosin is resin, but not all resin is rosin.
resole:	a thermosetting resin formed by reaction of phenol with formaldehyde in a ratio less than 1:1 under alkaline conditions. *Bakelite* (after Leo Baekeland, who invented it in 1907) is an example of the type. Compare *novolac.*
respirable:	fit for breathing, *e.g.*, uncontaminated oxygen gas
retrofit:	to furnish older equipment with new parts or design changes
rifted:	of solid particles, those that contain many cracks and cleavages and thus have greater surface area than their size would suggest
riser:	in foundry practice or plastics molding, a vertical channel on a mold that allows for escape of air and serves as a receptacle for excess material
Robbins-Monro test:	a test method similar to the Bruceton test (*q.v.*) but differing in that the step size decreases as 1/N where N is the sample currently tested. The test points are concentrated at the mean, hence it is very inefficient for determining any population parameter except for the desired probability, and ability to estimate reasonable confidence intervals for these parameters is severely limited.

Roman candle:	a cylindrical firework that contains multiple stars or other projectiles, together with their lifting or "blowing" charges and delay elements separating them
rondelle:	a type of timed explosive insert used in cylindrical firework shells. The word *rondelle* implies that the devices explode in a circle, but this does not always apply in practice.
round shell:	implies a spherical shell; the same applies to "round stars"
safety faker:	(*colloquial, often hyphenated*): a person who disseminates exaggerated or inaccurate safety warnings, whether due to fear of litigation, desire for personal gain, or simple ignorance. Safety-fakery is a widespread phenomenon in modern society, affecting fields ranging from medicine to automobile design. However, it is especially prevalent regarding chemicals, fireworks, black powder and anything that goes "bang!"
safety fuse:	a specialized kind of fuse consisting of black powder within a woven textile cord, and usually coated with a material such as asphalt or varnish. It is distinguished by a very regular burning rate and little or no "spit" of flame out the side. Compare *Bickford.*
safety pin:	a device resembling a cotter pin that locks movable parts of a fuze (as on a hand grenade) but is easily removed by means of a pull-ring, either by hand or by a lanyard
salute:	in fireworks or signalling, a device that produces a single loud explosion as its only significant effect
scavenger:	a material used to remove traces of a gas by chemical reaction
scoria:	slag or dross, especially when it is porous like the rock of the same name. The word is often applied to the "chimney" of residue produced by some flares when burning.
secondary explosive:	an explosive which requires a shock wave (as from a primary explosive) in order to detonate – for all practical purposes, a synonym for *high explosive*

serpent:	a small tubular firework item that contains rammed composition and usually a choke or nozzle, and produces enough thrust to move under its own power. Serpents may be fired singly on the ground but today they are usually used in shells or mines.
setback:	apparent rearward motion due to inertia, as occurs in launching a projectile
shaped charge:	a high explosive charge of special configuration that produces very high penetration for its size, also called a "lined cavity charge," or a "Munroe charge." The term should not be rendered "shape charge."
shelf item:	something made and put in storage for prospective customers before an order is received. In pyrotechnics shelf items are rarely made, except for standardized commercial products.
shelf life:	length of time in storage during which an item will remain in serviceable condition; a synonym for *storage life*
shell:	a hollow projectile containing an explosive bursting charge. The resemblance between military and firework types is readily apparent, and was even closer in the past. In warfare, the verb *to shell* means to attack an enemy with artillery of this type. For sporting weapons the word is often used in a looser way to refer to a complete round of ammunition that does not contain an explosive projectile, *i.e.*, ".22 shells" or "shotgun shells."
shell-of-shells:	in fireworks, a shell that contains multiple smaller shells, usually of the same general shape. Cylindrical inserts fit best in cylinder shells, while inserts for ball shells are usually spheroidal.
silicon:	a non-metallic element, atomic number 14, in the same chemical family as carbon
silicone:	any of a class of polymeric organic silicon compounds containing the Si-O group, commonly used as lubricants, sealants or electric insulators

simulator:	an item that more or less harmlessly imitates a hazardous device, and is used for training purposes
single-base:	refers to smokeless propellants that contain nitrocellulose as their only active ingredient
slow match:	cordage treated with a solution of potassium nitrate or other substances, to cause it to smoulder slowly once ignited; used in the past as a source of fire, *e.g.*, to fire cannon or ignite fireworks, as punk is used today. Compare *quickmatch*.
smoke:	in pyrotechnics, an ærosol of chemical particles or droplets used for obscuring objects ("screening") or for signalling
smokeless:	refers to propellants based on nitrocellulose, with or without other active ingredients such as nitroglycerine. Powders of this type actually produce a small amount of smoke, but far less than black powder, which was the original basis for comparison.
sofar bomb:	an explosive device designed to detonate at a specific depth in the sea
specific impulse:	the impulse generated per unit mass of propellant
specification:	an attempt to describe an item and its expected functioning so that anyone skilled in "the art" can produce it
spider:	a firework shell that produces a strong burst of streamer stars. Traditionally, *spider* or *spiderweb* implies the use of charcoal-based stars producing a soft golden effect, but the term is also applied to metallized versions, *e.g.*, "white spider" or "glitter spider."
spiking:	in firework making, refers to the technique of winding shells with twine to increase their strength. The word is derived from the Italian *spago*, meaning string.
splitting comet, *also* **split comet:**	see *crossette*
spontaneous:	occurring without external energy input. Spontaneous ignition is normally one of the greatest fears of

pyrotechnists and all practical steps are taken to avoid it. However, the phenomenon can be used deliberately in such devices as igniters used for sabotage of enemy property.

squib:	broadly, a small tube or packet of pyrotechnic composition used for any of several purposes, including ignition of larger devices. Formerly, the word was commonly applied to fireworks of the serpent class, and also to a type of mild black powder firecracker that did not produce a loud noise unless further confined. Today, *squib* usually means a small electrically-fired igniter containing an *electric match* (*q.v.*).
star:	a consolidated pellet of pyrotechnic composition, designed to be released from a larger device. A star may produce a single point of colored light, or a trail of sparks, or both. The term normally implies an ærial device, but small stars may also be discharged by fountains and similar ground fireworks.
stoichiometry:	refers to precise balance of weights of materials in a reacting mixture. A pyrotechnic composition that reacts completely, leaving neither excess oxygen nor significant amounts of unreacted fuel, is said to be stoichiometric.
strategic material:	a material needed for the industrial support of a war effort (compare *critical material*)
streamer:	a star that leaves a visible trail of burning material as it moves through the air: a "tailed" or "tailing" star
subsieve size:	of a particle size too small to be separated and characterized by so-called standard sieves. This usually means below about 43μ particle diameter; in pyrotechnics some materials have only 1 to 10μ average particle size.
surveillance:	originally a term for close watchfulness, it has assumed the meaning of observation of ordnance items under severe test conditions
TBI:	*through bulkhead initiator*: an explosive device which initiates a propellant or pyrotechnic mixture by shock transmitted through a bulkhead while maintaining confinement

temperature coefficient:	the relative change of some measurable quantity (*e.g.*, burning time per unit length) with change of temperature, usually expressed as mean change per degree in percent of mean temperature with a given range
thermate:	an incendiary composition consisting of thermite with additives, such as barium nitrate
thermite:	specifically, a mixture of granular aluminum and black iron oxide that produces molten iron at a very high temperature. Today the term is more broadly applied to any comparable mixture of a metal powder with the oxide of a less reactive metal. The original *Thermit* was a proprietary name.
TGA:	*thermogravimetric analysis*: an instrumental method for measuring the loss of mass from a compound or mixture, as a function of temperature and time. Differential thermogravimetric analysis (DTGA) is a powerful tool for the study of reaction kinetics.
torpedo:	**1:** an explosive weapon used for destroying ships, specifically, an elongated, self-propelled device that can be aimed or directed from a distance. **2:** a small explosive firework activated by impact or crushing, rather than by a fuse. **3:** an explosive signalling device designed to be attached to a railroad track and fired by a train's weight, usually called specifically a *railway torpedo.*
tourbillion:	an ærial firework that spins in a horizontal plane and rises under its own power, really a type of rocket, although it is never called one in practice. In the United States the terms "helicopter" and "buzz bomb," derived from popular brand names, have become the usual generic labels for tourbillions.
tremalon:	(from Italian, *tremolante* or *flickering, twinkling*) a firework effect characterized by combustion which forms a glowing semi-reacted dross; this semi-reacted dross, as it falls or is propelled through the air, reacts to completeness, emitting flashes. Synonymous with American *flitter*, def. 2 (*q.v.*) and British *glitter* (*q.v.*).

vehicle:	a liquid or semi-solid in which particles or droplets of active material are dispersed
Very pistol:	a type of flare pistol introduced in the mid-nineteenth century and named for its inventor Edward W. Very (*d.* 1910). Although it is not really correct, many people continue to apply the term to all types of flare pistols.
vitiate:	to debase or make faulty; used especially of air having reduced oxygen content
volatile:	readily evaporable; having a relatively high vapor pressure under standard conditions. It is a vulgar error, to be noted with regrettable frequency in the popular press, to use this word as a synonym for *unstable, explosive,* or *flammable.*
warimono:	(Japanese) a type of spherical shell characterized by a relatively thickly-papered case and a relatively large burst charge, designed to form a spherical burst pattern of relatively fast-burning stars, which expire at the periphery of the sphere before their trajectories appear to droop visibly under the influence of gravity. *Chrysanthemum* (*q.v.*) and *peony* (*q.v.*) shells are examples of the *warimono* type.
willow:	a relatively soft burst of tailed stars, as from a shell or rocket, which produces a drooping pattern resembling a willow tree. Compare *poka* (*q.v.*).

Appendix I

Selected Further Resources for Pyrotechnics

1. Organizations

American Pyrotechnics Association
Julie Heckman, Executive Director
P.O. Box 30438
Bethesda, MD 20284-0438
[4606 Mooreland Lane, Suite 109, Bethesda, MD 20814]

Tel.: (301) 907-8181
Fax: (301) 907-9148

e-mail: jheckman@americanpyro.com

American trade association for domestic manufacturers and importers of fireworks; supplies educational materials for firework safety. Tries to defuse the most egregious errors stated about fireworks accidents disseminated on national news media, usually by CPSC and other federal agencies.

Energetic Components and Systems Technical Committee (ECS TC) of the
American Institute of Aeronautics and Astronautics (AIAA)
Thomas J. Blachowski, ECS TC Secretary
Indian Head Division
Naval Surface Warfare Center
101 Strauss Avenue
Indian Head, MD 20640-5035

Tel.: (301) 744-2362
Fax: (301) 744-4881

e-mail: blachowskitj@ih.navy.mil
website: www.aiaa.org/tc/ecs/index.html

Holds symposia and meetings.

The International Pyrotechnics Society
Dr. B. R. Hubble, Secretary
P.O. Box 2
Bloomfield, IN 47424
Tel.: (812) 854-4053
e-mail: hubble_bill@crane.navy.mil
website: www.intlpyro.com

Professional society promoting research and education in the field of pyrotechnics. Sponsors the International Pyrotechnics Seminars. For information on next IPS Seminar, see [www.intlpyro.org/IPS28].

Pyrotechnics Guild International, Inc.
Ed Vanasek, Secretary/Treasurer
18021 Baseline Avenue
Jordan, MN 55352
Tel.: (952) 492-2061
e-mail: edvanasek@aol.com
website: www.pgi.org

The PGII, founded in 1969, is an independent, worldwide, nonprofit organization of amateurs and professional fireworks enthusiasts.

National Fireworks Association
8224 N. Bradford Court
Kansas City, MO 64151
Tel.: (816) 505-3589
website: www.nationalfireworks.org

The NFA is a trade association which monitors government regulation of fireworks, fights restrictive legislation, organizes trade shows, and promotes the positive image of the fireworks trade.

[NOTE: Two of the above listed organizations, the International Pyrotechnics Society and the Pyrotechnics Guild International, Inc., also publish serials. The PROCEEDINGS of the IPS appear whenever a seminar is held. The Pyrotechnics Guild International, Inc. publishes the PGI BULLETIN five times a year.]

2. Publications

Chemical Publishing Company, Inc.
192 Lexington Avenue, Suite 1201
New York, NY 10016-6823
Tel.: (212) 779-0090
e-mail: chempub@aol.com
website: www.chemicalpublishing.com

Publisher of George W. Weingart's *Pyrotechnics*, Herbert Ellern's *Military and Civilian Pyrotechnics* and Rev'd. Ronald Lancaster's *Fireworks: Principles and Practice*.

COMBUSTION AND FLAME
The Combustion Institute
5001 Baum Blvd., Suite 635
Pittsburgh, PA 15213-1851
Tel.: (412) 687-1366
Fax: (412) 687-0340
e-mail: combust@telerama.lm.com

Publication of an educational, non-profit, international, scientific society, the purpose of which is to promote and disseminate research in combustion science.

EXPLOSIVES AND PYROTECHNICS
Franklin Applied Physics
P.O. Box 313
Oaks, PA 19456
Tel.: (610) 666-6645
Fax: (610) 666-0173
e-mail: frankphys@aol.com

Monthly newsletter of explosives, pyrotechnics and their devices, training courses, RF training.

High Power Rocketry
P.O. Box 970009
Orem, UT 84097-0009
Tel.: (801) 225-3250
Fax: (801) 225-9307
website: www.tripoli.com

Prometheus Publications
P.O. Box 7584
Phoenix, AZ 85011
Tel/Fax: (602) 553-3698
e-mail: prometheus_pubs@hotmail.com

"New, used, out-of-print and rare books on pyrotechnics. Fireworks-related graphic art. Always seeking to obtain unusual literature from single pieces to entire collections."

PROPELLANTS, EXPLOSIVES, PYROTECHNICS (PEP)
North, Central and South America Customer Service
John Wiley & Sons, Inc.
605 Third Avenue
New York, NY 10158-0012
Tel.: (212) 850-6645
Fax: (212) 850-6021
e-mail: subinfo@wiley.com

Published six times a year, this international journal provides a vital forum for the exchange of ideas in the areas of propellants, explosives, primers, and pyrotechnics, and combustion and detonation processes.

Pyrotechnica Publications
P.O. Box 611
Post Falls, ID 83877-0611
Phone/Fax: (208) 664-0388
email: pyropubs@aol.com

Publishers of the ongoing series, PYROTECHNICA: OCCASIONAL PAPERS IN PYROTECHNICS. Seventeen issues since 1977. Publishers of Dr. Takeo Shimizu's *Fireworks: The Art, Science, and Technique*, Shimizu's *Fireworks from a Physical Standpoint*, and Dr. Alexander P. Hardt's *Pyrotechnics*.

THE FIREMAKER
Larry Homan, publisher
P.O. Box 162
Fresno, CA 93707
e-mail: lhoman@earthlink.net

"An interesting journal for the pyrotechnically enthusiastic." Emphasis on fireworks.

3. Services and Supplies

Ace Paper Tube Corporation
4918 Denison Avenue
Cleveland, OH 44102
Tel.: (216) 961-0250
Fax: (216) 961-1114

Manufacturer of paper tubes, discs, and other paper products for the fireworks industry.

Austin Powder Company
430 Powder Plant Road
McArthur, OH 45651

Tel.: (740) 596-5286
Fax: (740) 596-4050

website: www.austinpowder.com

Full line of high explosives and initiating devices.

Autoliv ASP, Inc.
Headquarters
3350 Airport Road
Ogden, UT 84405

Tel.: (801) 625-9200
Fax: (801) 625-4911

website: www.autoliv.com

Airbag manufacturer.

B.F. Goodrich Aerospace
Universal Propulsion Company, Inc.
25401 N. Central Avenue
Phoenix, AZ 85027-7837

Tel.: (623) 516-3340
Fax: (623) 516-3364

Manufacturer of ejection seats, slides, airbag inflators.

Brunchu Hnos. S. L.
Carrer Major, 86
46110 Godella
Valencia
Spain

Tel.: (34) 96-3638010
Fax: (34) 96-3641213

e-mail: correo@brunchu.com
website: www.brunchu.com

Manufacturer, distributor, importer/exporter of display fireworks, consumer fireworks, and special effects.

CANMET – Canadian Explosives Research Laboratory
555 Booth Street
Ottawa, ON K1A OG1
Canada

Ron Vandebeek, manager
Tel.: (613) 995-1275
Fax: (613) 995-1230

Laboratory work and testing, provides "safety standards" for explosives and fireworks; sponsors the "International Symposium on Fireworks."

Cartridge Actuated Devices
123 Clinton Road
Fairfield, NJ 07004-2991

Tel.: (973) 575-1312
Fax: (973) 575-6039

Manufacturer of explosive bolts, cable cutters, squibs, and valves.

Cienfuegos, Ltda.
R. Cel. José Batista dos Santos, 72 - Centro
35560-000 Santo Antônio do Monte
Minas Gerais
Brazil

Tel.: (037) 281-2279
Fax: (037) 281-1670

The Brazilian factory of the Argentine-based firm where display and consumer fireworks are manufactured with Chinese manufacturing techniques.

Daveyfire, Inc.
500 Yanogo Valley Road, Suite 250
Walnut Creek, CA 94596

Tel.: (925) 926-6412
Fax: (925) 926-6439

e-mail: daveyfire@msn.com
website: www.daveyfire.com

Manufacturer of initiation devices and components.

Dongguan Native Produce Import/Export Co. of Guangdong
No. 14 Guangming Road
Guangzhou County
Guangdong Province
Dongguan 511700
China

Tel.: (86) 769-224-8991
Fax: (86) 769-221-2921

e-mail: bnxeco@pub.dgnet.gd.cn

Manufacturer and distributor of display and consumer fireworks.

Elephant Black Powder
7650 U.S. Highway 287, Suite 100
Arlington, TX 76001

Tel.: (817) 478-8888
Fax: (817) 478-8891

e-mail: petro@fastlane.com

Importer of Elephant black powder from Brazil; squibs, fuse, detonation cord.

Explosive Special Effects
10510 El Comal Drive
San Diego, CA 92124

Tel.: (619) 565-0684
Fax: (619) 565-6440

Pyrotechnic special effects and theatrical operations, indoor and outdoor.

Fireworks by Grucci
One Grucci Lane
Brookhaven, NY 11719

Tel.: (613) 286-0088
Fax: (613) 286-9036

e-mail: info@grucci.com
website: www.grucci.com

Manufacturer and importer of display and consumer fireworks; special effects pyrotechnics, custom designers of displays and performances.

Franklin Explosive Safety
1518 Noble Road
Rydal, PA 19046
Tel.: (215) 887-9211
Fax: (603) 761-7033
e-mail: Franklinexplsafe@yahoo.com
website: http://members.home.net/pandrthompson/
Consulting on RF safety and other EED problems.

Garden State Fireworks, Inc.
P.O. Box 403
Millington, NJ 07946
Tel.: (908) 647-1086
Fax: (908) 647-6258
Manufacturers of display fireworks, display producers.

GOEX, Inc.
P.O. Box 659
Doyline, LA 71023-0659
Tel.: (318) 382-9300
Fax: (318) 382-9303
Commercial and military black powder.

Halliburton Energy Services
Jet Research Center
8432 S. Interstate Highway 35 West
Alvarado, TX 76009-9775
Tel.: (800) 451-5403
Fax: (817) 783-5812
e-mail: James.Barker@halliburton.com
Shaped charges, DDT detonators, detonation cord.

Hands Fireworks, Inc.
R.R. #4
Prescott, ON KOE 1TO
Canada
Tel.: (613) 925-2832
Fax: (613) 925-1207

Manufacturer of display and consumer fireworks, special effects, and military pyrotechnics.

Hodgdon Powder Co., Pyrodex Division
P.O. Box 2932
Shawnee Mission, KS 66201
Tel.: (913) 362-9455
Fax: (913) 362-1307

Pyrodex powder and pellets, compacted charges and other pyrotechnic compositions.

Hosoya Fireworks Co., Ltd.
1847 Sugao
Akiruno-city
Tokyo 197-0801
Japan
Tel.: (81) 42-559-2578
Fax: (81) 42-559-2413
e-mail: hosoya-rdc@pop16.odn.ne.jp

Manufacturer and exporter of display fireworks (shells) and consumer fireworks.

Hummel-Croton, Inc.
10 Harmich Road
South Plainfield, NJ 07080-4899
Tel.: (908) 754-1800
Fax: (908) 754-1815

Manufacturer and distributor of chemicals for the pyrotechnics and fireworks industries.

Jakob Hatteland Kjemi A/S
N-5578 Nedre Vats
Norway
Tel.: (47) 52-76-30-28
Fax: (47) 52-76-51-09
e-mail: jakob/jhe-h@hatteland.no
website: www.hatteland.no

Manufacturer and importer of display fireworks; electronically fired shows using computerized choreography.

Kimbolton Fireworks, Ltd.
7 High Street,
Kimbolton, Huntingdon
Cambs. PE18 OHB
England UK

Tel.: (44) 1480-860988
Fax: (44) 1480-861277

e-mail: markl@kim-fireworks.demon.co.uk
website: www.kim-fireworks.demon.co.uk

Manufacturer, importers and exporters of display fireworks and shop goods; display operators.

Komatsu Fireworks Co.
Omagari City
Akita Province
Japan

Manufacturer of display fireworks.

Lacroix-Ruggieri
6 blvd. Joffrery
31607 Muret Cedex
France

Tel.: (33) (0) 5-61-56-65-00
Fax: (33) (0) 5-61-56-64-96

Manufacturer, importer/exporter, and distributor of display fireworks, special effects, pyrotechnic devices for defense and industry.

Legion Fireworks Co., Inc.
90 Chelsea Road
Wappingers Falls, NY 12590

Tel.: (914) 831-8328
Fax: (800) 977-PYRO

e-mail: frankc696@aol.com
website: www.legionfireworks.com

Manufacturer, distributor, importer/exporter of display fireworks.

Lidu Export Fireworks Factory
Lidu Town, Jinxian County
Jiangxi Province,
Nanchang, Jiangxi 311725
China

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Fax: (86) 791-563-8138

e-mail: dgm@public.nc.jx.cn
website: www.lidu.firework.com

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14149- 32nd Street
Buffalo, ND 58011

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Fax: (701) 633-5352

e-mail: lightnpyro@yahoo.com

Manufacturer of colored smokes, screening smokes, æronautical smokes; bulk supplier of chemicals for the fireworks industry.

Luna Tech, Inc.
148 Moon Drive
Owens Cross Roads, AL 35763

Tel.: (256) 725-4224
Fax: (256) 725-4881

e-mail: sales@pyropak.com

Manufacturer of Pyropak® pyrotechnic products; indoor special effects.

Mapcoa, Inc.
4868 Chaincraft Road
Cleveland, OH 44125

Tel.: (216) 587-5688
Fax: (216) 587-3764

Manufacturer and supplier of magnesium/aluminum alloy powders.

Marutamaya Ogatsu Ltd.
4-5-12 Nihonbashi Honcho
Chuo-ku, Tokyo 103
Japan

Tel.: (81) 03-3241-6538
Fax: (81) 03-3275-0062

Manufacturer of display fireworks (shells).

MP Associates, Inc.
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Fax: (209) 274-4843
Manufacturer of special effects; R&D, testing.

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via Oberdan, 105
45037 Melara, Rovigo
Italy
Tel.: (39) 0425-89035
Fax: (39) 0425-89640
Manufacturer of display fireworks; display producers.

PerkinElmer Optoelectronics
Technical Information
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Tel.: (937) 865-5586
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Mexico, D.F. 07840
Mexico
Tel.: (52) 55-37-10-56
Fax: (52) 55-17-41-93
e-mail: ventas@pirotecniainternacional.com
website: www.pirotecniainternacional.com

Manufacturers and distributors of display fireworks and special effects, display operators.

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10041 Carignano
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Manufacturer of display fireworks and pyrotechnics for the military.

Pirotecnia Zaragozana, S.A.
Paseo Maria Agustin, 4-6
Zaragoza
Spain
Tel.: (34) 976-44-08-99
Fax: (34) 976-43-91-63

Manufacturer of display fireworks.

Pyrodigital Consultants
1074 Wranglers Trail
Pebble Beach, CA 93953
Tel.: (831) 375-9489
Fax: (831) 375-5225
e-mail: pyrodig@aol.com

Manufacturer of computerized firing systems and choreography equipment for fireworks displays.

Pyro Spectaculars, Inc.
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Rialto, CA 92377
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Fax: (909) 355-9813
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Schönauerstrasse, 150
Austria
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Fax: (43) 318-53-41

Manufacturer of display fireworks, display producers.

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Fax: (847) 925-8120

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WECO Pyrotechnische Fabrik GmbH
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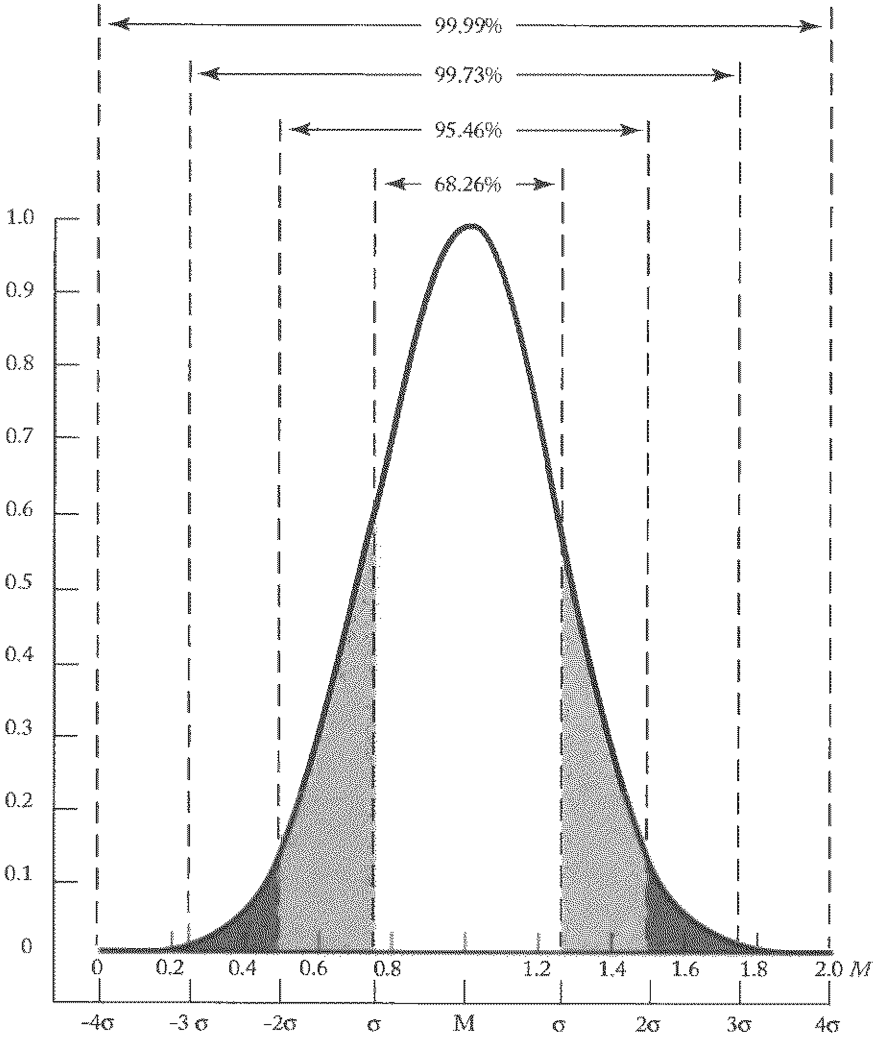
Manufacturer of display fireworks, consumer fireworks, and special effects.

Appendix II

Normal Distribution, Mean, and Standard Deviation



The Normal Distribution Curve

NORMAL DISTRIBUTION, MEAN, AND STANDARD DEVIATION

When a sample quantity of pyrotechnic articles is tested, and the results of the test are plotted on a graph where the x-axis represents the value measured (*e.g.*, seconds of burning time, centimeters of drop required to initiate a composition using a 2-kilogram weight) and the y-axis represents the number of measurments, a bell-shaped curve results. If the apex of this curve is centered on the *mean*, it represents a *normal* or *Gaussian* distribution ideally represented in the illustration. If not centered on the mean, the distribution is described as *skewed*.

The mean, μ or $\bar{x}$, is an arithmetic average computed by adding the values, x, measured, and dividing by the total number of measurements, n.

$$\mu = \frac{x_1 + x_2 + \ldots x_n}{n}$$

The *variance*, σ^2, of a sample of n values is defined as the sum of the squares of the deviations from the sample mean divided by $(n - 1)$. The *standard deviation*, σ, of a distribution is the square root of its variance:

$$\sigma = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \ldots (x_n - \bar{x})^2}{(n - 1)}}$$

This parameter defines the fraction of area under a normal distribution curve as follows:

Number of Standard Deviations measured + or − from the Mean	Percent of Area
0.675	50.00
1.00	68.26
2.00	95.46
3.00	99.73
3.48	99.95
3.89	99.99

Appendix III

Sieve Sizes

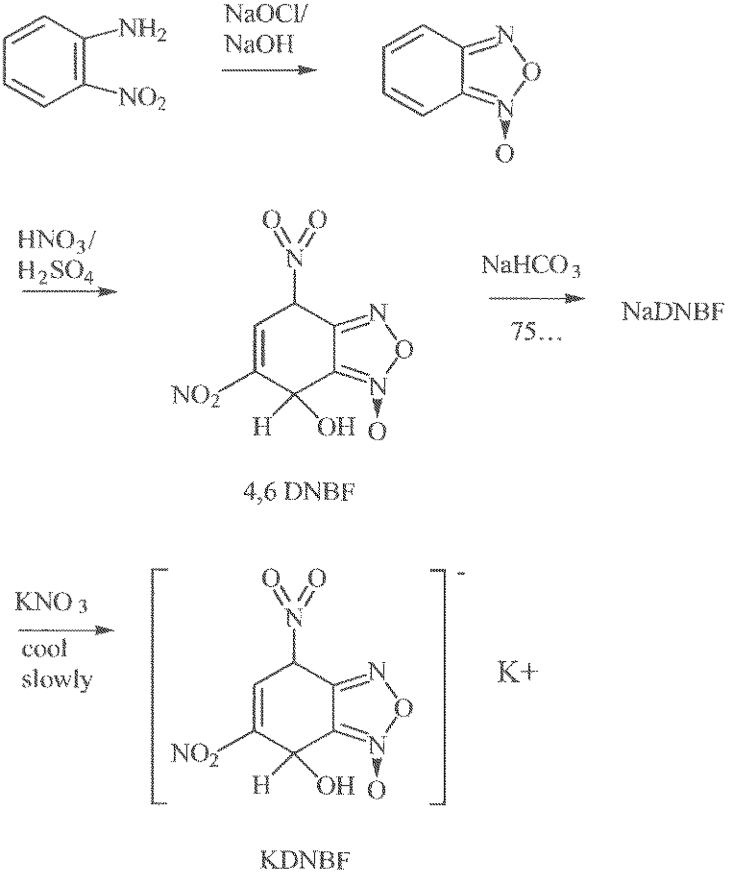
Components of pyrotechnic mixtures are often specified in standard mesh sizes, or as having passed through one (−) but having been retained on a smaller (+) size; *e.g.*, "−120, +200 mesh." The higher the mesh number, the smaller the particle size. The standard sieve dimensions described by mesh numbers are as follows:

Mesh Number	mesh opening µm	wire dimension µm
100	147	107
120	124	97
140	104	66
170	88	61
200	74	53
230	61	41
270	53	41
325	43	36
400	38	25

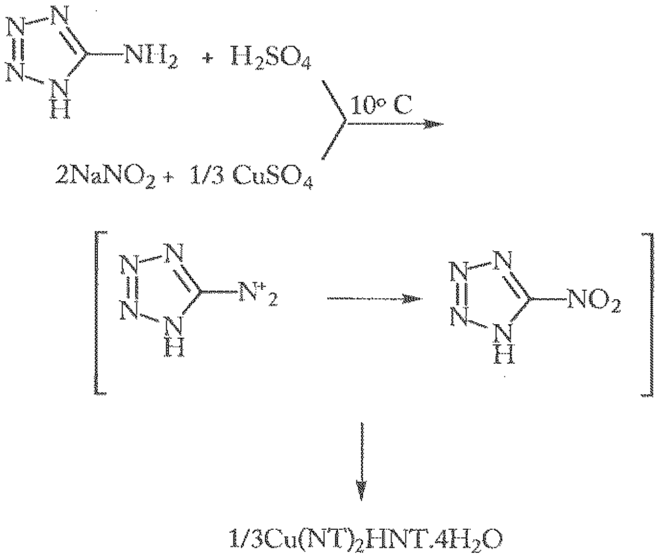
Pyrotechnic components in the <43 µm range are said to be sub-sieve size.

Appendix IV

KDNBF and DXN-1 (DXW-1)



Synthesis of Potassium Dinitrobenzotrifuroxan.[159]

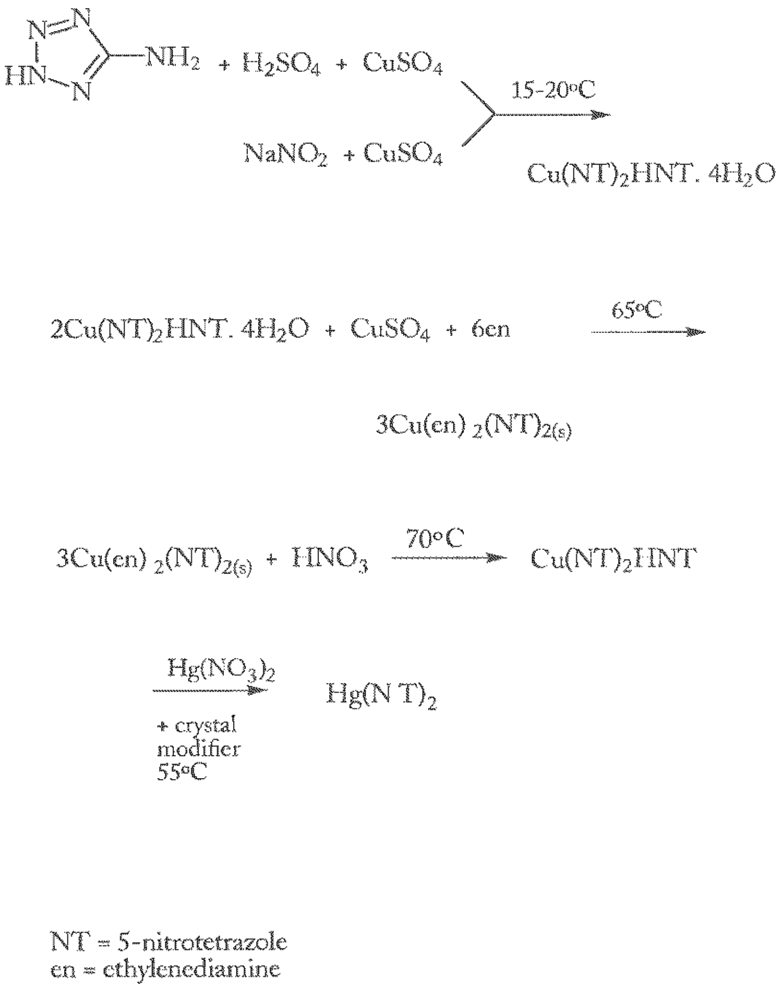


$$Cu(NT)_2HNT.4H_2O + 3NaOH \longrightarrow CuO_{(s)} + 3NaNT$$

$$2NaNT + Hg(NO_3)_2 \longrightarrow Hg(NT)_2 + 2NaNO_3$$

"NT" = "5-Nitrotetrazole"

Von Herz Synthesis of Mercuric 5-Nitrotetrazole.[159]



NT = 5-nitrotetrazole
en = ethylenediamine

PERME Process for Manufacture of Mercuric 5-Nitrotetrazole with improved yield over Von Herz Synthesis.[159]

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A Note on the Type and Printing

The text of this book is set in Adobe Caslon, enhanced with the typographic refinements of the Adobe Caslon Expert Collection. It takes its name from William Caslon (1692-1766), the great English letter-founder. Prior to Caslon's time, most of the printing types used in Britain had been imported from the Netherlands, and British printing had little distinct national character. Caslon had been apprenticed to an engraver of gun-locks and barrels, and later did silver-chasing and cut tools for bookbinders, prior to taking up the type-founding business. Grace and legibility without distracting ornament are the hallmarks of his designs.

Adobe Caslon is patterned after American Type Founders' Caslon Old Style 471, among the most faithful reproductions in modern times of the types shown in Caslon's Specimen of 1763, the first type specimen-book issued in England.

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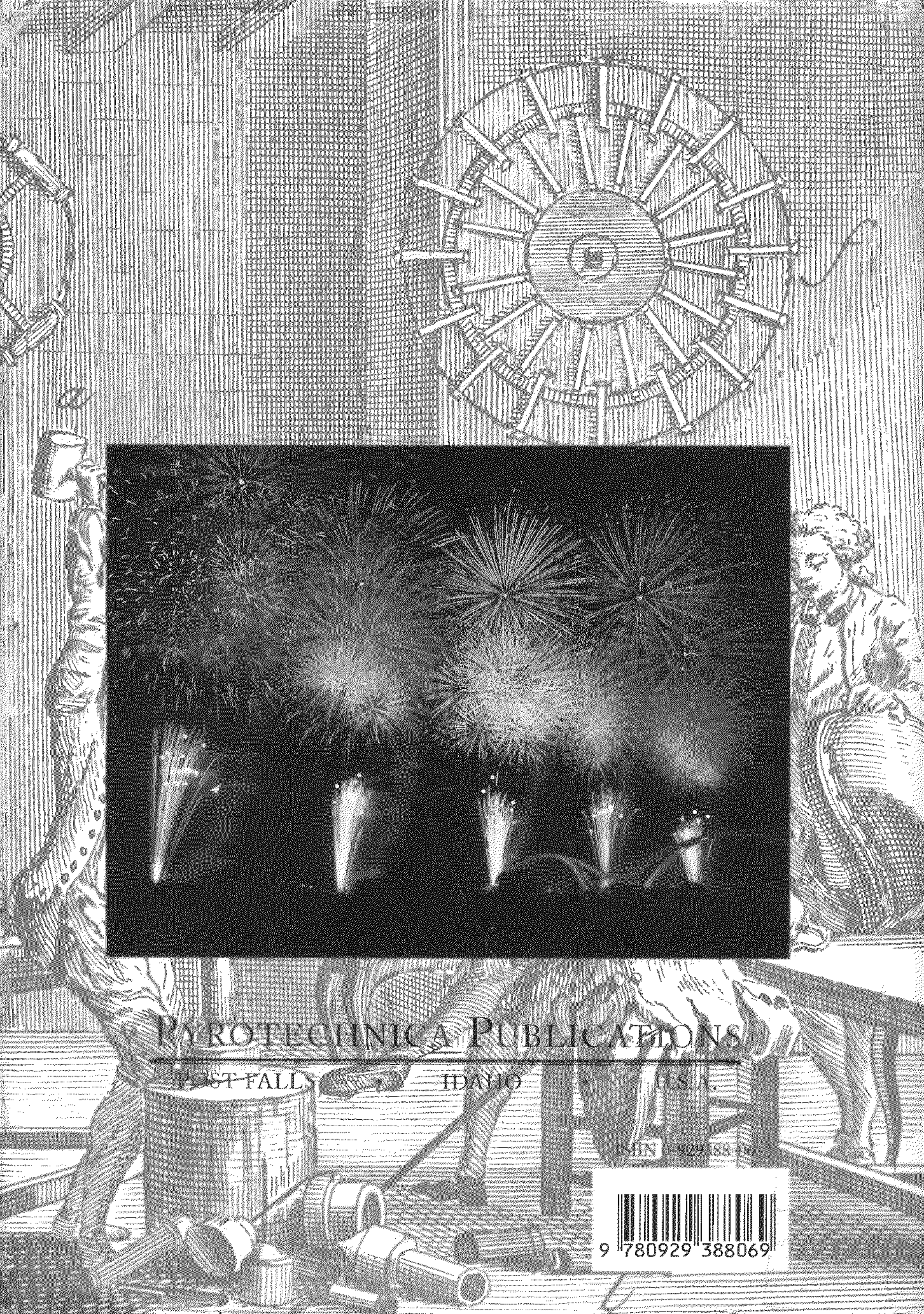

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